Feasibility of Decontaminating Dredged Material

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Report SR 546
February 1999

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Summary

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The sediment commonly found on the bed of lakes, rivers, estuaries and coastal zones is often contaminated through the activities of man. Where it is found in ports and navigation channels it may have to be removed to maintain access for shipping. Less frequently, but also importantly, there is a need to remove such sediment for environmental reasons, sometimes termed "clean-up", for example to improve amenity value of waterways no longer required for shipping. Whether the contaminated material arises from capital dredging, maintenance dredging or clean-up dredging it is termed "contaminated dredged material" (CDM), for the purpose of this report. The CDM will require either treatment, to make it safe for beneficial use or disposal, or isolation (for example in a confined disposal facility). This report is only concerned with treatment.

The research leading to this report followed a review of the feasibility of decontaminating dredged material carried out in 1995-96 under DoE Contract CI 39/5/94 (Fletcher and Burt, 1996). The report noted that increasingly there are cases in the UK where dredged material is contaminated to the extent that disposal options are restricted and costly containment at commercial landfill sites is required. In other parts of the world much greater contamination occurs and serious problems exist which can be addressed by the UK. The report went on to recommend further work to investigate the effectiveness and suitability of promising decontamination technologies over a range of sediment types and contaminant mixes.

This report investigates the treatment technologies that are already available and assesses their applicability including costs. It also investigates new technologies and identifies those that have the potential for further development. It reviews and highlights research occurring around the world notably in the USA, Canada and the Netherlands while the Appendices describe pilot studies. A list of firms and their technologies offered have been included in this report. The list is not exhaustive and any inclusion or omission of particular companies should not be taken as either endorsement or criticism respectively.

A wide variety of treatment techniques are available for contaminated dredged material. The currently available techniques can destroy, remove or immobilise a wide range of contaminants and are applicable to almost all types of dredged material. The costs are still high but are decreasing.

Full scale separation and dewatering techniques are already being used internationally to good effect. Flotation and gravitational separation are very promising, lower cost techniques that have been used successfully at a number of sites. In particular one plant installed in Hamburg, Germany is processing close to

Summary continued

1 million tonnes/year of sediment in this way and is recycling much of the processed material.

Thermal treatment technologies have been used at a number of very highly contaminated sites in North America with success but at high cost.

Biological remediation appears to offer the most cost-effective treatment for organic contaminants. Landfarming and bioslurry treatment are likely to be the most cost effective but it may prove difficult to achieve target residual levels. The targets should be reviewed in the light of what is reasonably achievable and what genuinely constitutes a threat to the environment.

Each dredging problem involving contaminated material is a unique situation that demands a custom tailored solution. For each site, the optimal combination of treatment technology must be determined by weighing technical, economic, social and environmental factors.

The present situation is that most contaminated dredged material in the developed countries is dealt with by placing it in confined disposal sites either on land or in subaqueous pits. In many developing countries any special handling is regarded as an unaffordable luxury and marine disposal continues in contravention of international conventions and guidelines.

In most countries the availability of such disposal sites is not likely to meet future demands. Inevitably the lack of disposal site capacity has to be offset by the full scale use of options such as treatment, sand beneficial uses of dredged material. These should become the predominant choices for future dredging operations.

Furthermore the contaminated materials in many existing disposal facilities will have to be reclaimed in order to restore capacity and to meet public demand.

There is thus a demand for cost-effective treatment on a large scale. At present the ports face an unfair share of the responsibility for the remediation and placement of contaminated sediments. Perhaps the responsibility should be shared nationally. Various international and national policies incorporate the "polluter pays" principle. However, faced with diverse contaminants from numerous sources, both historic and present day, it seems like an impractical, tedious and costly if not impossible scenario in most cases. Upstream generators of contaminants often cannot be identified or held accountable, leaving ports to manage the problem. Historically some actions have been ignorant of the consequences of a careless attitude to waste disposal. It has wrongly been assumed that the assimilative capacity of the aquatic environment was infinite. It seems reasonable that the costs of cleaning up historic contamination should be shared.

The only long-term and cost effective solution has to be control of pollution at source. In the meantime governments and industry should work together to develop technologies capable of cleaning up the mess. Taxes on existing polluters is one way of generating funds for research and development. In the USA the "Superfund" has financed several demonstration projects. In the UK the "landfill tax" was also intended to generate funds. However, the uptake so far has been small and rules governing research grants lack flexibility, requiring, for example, that the researcher has to be based at a site within a certain distance of a landfill site.

The size of the problem in the UK is not large. However, taking a view of Europe, particularly Eastern Europe with it, many heavily polluted inland waterways, there would appear to be a considerable market for cost effective technologies. There is no doubt the UK organisations have the necessary skills to carry out the development but, other than for primary separation and dewatering treatment, the financial risk of development is high. There is a strong case for government investment in technology development.

The results of the bench scale, pilot scale and occasional full scale trials investigated in the context of this research project give sufficiently positive indications to justify further research and development initiative in the UK.

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1. INTRODUCTION

1.1 Background

The sediment commonly found on the bed of lakes, rivers, estuaries and coastal zones is often contaminated through the activities of man. Where it is found in ports and navigation channels it may have to be removed to maintain access for shipping. Less frequently, but also importantly, there is a need to remove such sediment for environmental reasons, sometimes termed "clean-up", for example to improve amenity value of waterways no longer required for shipping. Whether the contaminated material arises from capital dredging, maintenance dredging or clean-up dredging it is termed "contaminated dredged material" (CDM), for the purpose of this report. The CDM will require either treatment, to make it safe for beneficial use or disposal, or isolation (for example in a confined disposal facility). This report is only concerned with treatment.

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The follow up work began with a much more detailed review of contaminants, in particular their origins and the concerns about them. This was important because not all contaminants give reason for concern and the research should focus on those that may cause harm and require treatment (or isolation). This review is covered in Chapter 2.

It was hoped that this follow-up research would include a pilot scale study of a particular method of treatment. A particular problem had been identified with material dredged from the River Tees and the co-operation of a number of organisations had been provisionally agreed. However, between the early consultations and the award of the research contract virtually all of the organisations concerned had undergone some form of change: The National Rivers Authority had become the Environment Agency, Northumbrian Water had been bought by a French consortium and Tees and Hartlepool Port Authority had been sold off to private ownership. In the event, despite the personal support of the individuals concerned, it was not possible to get the higher level agreement necessary to make the project viable.

However, other projects were emerging and HR Wallingford took every opportunity for involvement. One project involving a field trial of the elctrokinetic method for removing mercury from canal sediments enabled HR to undertake a monitoring and reporting role (Appendix 1).

Co-operation from the US Environmental Protection Agency provided the opportunity to inspect remediation facilities in the US at first hand and provided access to a very large amount of data concerning the problems and the results of remediation trials.

The projects with which HR had a direct contact are described in the Appendices.

The other significant sources of information were conferences and seminars. HR took opportunities to present the results of the initial review and seek the views of co-workers in the field worldwide. The International Conference on Contaminated Sediments, held in Rotterdam in September 1997 was particularly relevant, and, more locally, one held by Imperial College gave the opportunity to discuss technologies with UK experts.

A number of firms offering remediation techniques have been contacted. Their information has been included, where appropriate, in the review of technologies in Chapter 3. A list of firms and the technologies offered is given in Appendix 6. The list is not exhaustive and any inclusion or omission of particular companies should not be taken as either endorsement or criticism respectively.

Chapter 4 discusses the factors affecting selection of a technology, including costs.

The preliminary findings were presented at a workshop held at HR Wallingford. The conclusions of that workshop have been taken into account in the overall conclusions of the research presented in Chapter 5.

1.2 Contaminated sediments

Sediments in rivers, estuaries and coastal regions have been contaminated by anthropogenic compounds for at least the last 100 years. The contaminants mainly adhere to the fine fraction of the sediment in suspension and settle to the bed in areas of, or at times in the tidal cycle, of low velocity.

Sediments comprise a mixture of assorted materials that have settled to the bottom of a water body often over the course of several years. Such material may include the shells and coverings of molluscs and other animals, transported soil particles from erosion, organic matter from dead and rotting vegetation and animals, sewage, industrial wastes, other inorganic and organic materials and chemicals (Mohan 1996).

Surface waters typically receive discharges of various liquid and solid wastes from three major sources:
- Point sources including municipal and industrial effluents;
- Non-point sources such as agricultural runoff, soil entrainment and airborne particles;
- Other sources such as spills, contaminated groundwater infiltration and intentional aquatic disposal.

Contaminants from these sources may include:
- Pesticides;
- Heavy metals;
- Nutrients;
- Oil and oil products;
- Organochlorine compounds;
- PAH's;
- PCB's;
- TBT

The sources and significance of these is discussed in some detail in Chapter 2.

1.3 Legislative and other controls

Most ports require maintenance dredging: many ports have had to provide greater depths to cater for modern shipping trends and this requires capital dredging to deepen channels and berths. In both cases considerable quantities of material may be generated and something has to be done with it. Dredged material management is controlled by a variety of international, regional, national and/or local treaties, laws, regulations and policies. International funding agencies also have their own environmental requirements. Detailed discussion of international and national systems is given in CEDA/IADC (1996).

Placement of dredged material at sea and on land fall under separate regulatory systems. Only marine disposal is covered by the international and regional conventions.

The most widely applicable international regulatory instrument for marine disposal is the London Convention (LC-72) which adopted the Dredged Material Assessment Framework (DMAF) in 1995. DMAF is widely accepted as a technically sound approach to the assessment procedure for placement at sea. It is reproduced in full in CEDA/IADC (1996). There are also regional conventions such as the Oslo-Paris Commission (OSPAR COM) and the Helsinki Convention.

Legislation controlling placement on land (and in inland waters) is based on national regulatory systems often involving a great variety of laws prepared for various waste materials (e.g. sewage sludge, agricultural and industrial waste). Some countries are now developing regulations specifically for dredged material.

1.4 Assessment of the material

There are three basic approaches to assessing the quality of the material and its suitability for disposal:

- **Standards**, whereby specified concentrations or total loads of contaminants are permitted;
- **Ecotoxicological**, whereby the toxic effects of the material are tested in a laboratory;
- **Case by case**, whereby each case is assessed in the context of the receiving environment (which may involve both other approaches).

A tiered approach is recommended by the US Environmental Protection Agency (USEPA) in which relatively easy and less expensive (but perhaps less definitive) tests would be conducted first with more sensitive tests to follow if necessary.

DMAF requires the consideration of possible beneficial uses of dredged material before disposal may be permitted. Previous research by HR Wallingford led to the production of guidelines for the beneficial use of dredged material (Burt 1997). Other significant guidance is given in PIANC (1992) and USACE (1986). The quality of the sediment clearly is of major significance whether the material is to be used in a beneficial way or disposed of, although the standards to be used in beneficial use schemes will vary according to the use proposed. If the material is found to be unsuitable for use then treatment may make it suitable. Similarly, if it is unsuitable for disposal, treatment may be the answer. Standards are discussed in Section 2.5.

1.5 Remediation

When a decision has been made that for environmental reasons the contaminated sediment in a port, river, or lake must be rendered harmless, four options are available:

- Cleaning the sediments in situ;
- Immobilising the contaminants in situ;
- Isolating the sediments in situ;
- Removal of the material followed by appropriate action such as:
  - Placement in a confined disposal facility;
  - Treatment – followed by beneficial use or disposal and safe disposal of any residue.

The main subject of this research project is "treatment" although other aspects are mentioned where the context requires it and a brief review of the other options is given here.

1.5.1 Natural recovery

Natural recovery, the reduction of contaminant concentrations through natural processes, is based on the practical observation that overall ecosystem recovery appears to be largely a function of time. Sediment decomposition and the mixing of new and old sediments by bottom dwelling organisms can both contribute to reducing contaminant concentrations. Knowledge of these processes is critical in the development of appropriate ecosystem recovery and waste management strategies. Evaluation to support natural recovery predictions are designed to collect and evaluate information necessary to determine whether surface sediment chemical concentrations, with adequate source control, will reach cleanup standards within a ten-year period (Garbaciak et al 1997).

This should always be considered as an alternative strategy for minimising biological damage. When using the no action strategy as a form of natural capping, consideration should be given to the length of time it takes for contaminants to become isolated from the food chain. It relies on the source of contamination having been eliminated and deposition of clean sediment. The clean sediment integrates with and remediates the contaminated sediment through dispersion, mixing, burial and biological degradation. A monitoring programme would be essential to ensure that the rates of contaminant release and the area of influence are acceptable (USEPA 1993).

The advantages of natural recovery are:
- Existing benthic habitat is not disturbed;
- Buried contaminants are not remobilised during remedial construction activities;
- Low cost.

The disadvantages include:
- Residual contamination is left in place and must be monitored;
- The alternative may not be viable in navigation areas which require maintenance dredging;
- The public may perceive it as a "do nothing" option, and may require education regarding the advantages of the approach.

USEPA states that it will not proceed with a clean up if a combination of pollution prevention and source controls will allow the sediment to recover naturally in an acceptable period of time (EPA 1994). The same policy states that the aggressiveness of a clean-up operation should be commensurate with the degree of risk. A process of sequential risk mitigation is described in Garbaciak et al (1997), based on three phases:

1. Immediately reduce the ecological and human health risks associated with high levels of contamination, using methods such as the confinement or capping of high risk materials;
2. Reduce the risks associated with moderate levels of pollution to a minimum, on a less urgent schedule and at lower cost;
3. Address areas of limited contamination through a combination of natural recovery and enhanced natural recovery (to aid or speed those natural processes).

1.5.2 In situ capping

This involves placing a layer of clean material evenly spread over contaminated sediments to provide isolation from the aquatic environment. The technique has been recognised by the London and OSPAR Conventions. It is much less expensive than land disposal or treatment (Clausner, 1994). The cap must be successfully placed, monitored and maintained. Considerations in evaluating the feasibility and eventual stability of the capped mound include water depth, bottom topography, currents, existing bed material and capping material characteristics and site capacity.

<u>Capping materials</u>: Clean sediments or soils are normally used. Other materials such as armour stone or geotextiles can also be incorporated.

<u>Cap thickness</u>: To provide sufficient chemical isolation, to prevent bioturbation and to account for potential erosion by currents, generally, a cap thickness of 50 cm to 1m is required. A thicker cap means more material but is easier to place. A balance in terms of the environment and economics need to be maintained.

<u>Long-term stability of capped mounds</u>: Long-term stability of capped mounds depends on consolidation and erosion processes. Differential settlement of capping and placed CDM may result in movement, deformation or even disruption of the cap.

<u>Placement techniques</u>: Accurate vessel location is essential. Detailed discussion of placement techniques is given in CEDA/IADC (in press). Technical guidance on design and implementation of capping projects is given in Palermo et al. (1998).

1.5.3 Confined disposal facility (CDF)

Depending on the intended level of isolation, confined disposal facilities (CDFs) fall in one of the following two categories:

- Simple facilities designed to retain dredged material solids;
- More complex facilities with controls to retain dredged material solids and all contaminants.

They may be water-based or land-based. Water-based facilities may be near-shore sites or island sites. Near-shore sites use the coast as one of the sides. CDFs may be constructed below or above the water table. CDFs above the water table are often called upland sites (US). Constructed dikes or natural or man-made pits may provide lateral containment (Rijkswaterstaat, 1992)

When dredged material is placed in the facility, the coarser fraction rapidly falls out near the inlet point and forms a mound. The fine-grained material continues to flow through the containment area and takes a long time to settle out. The clarified water and the water displaced by the dredged material are discharged over a weir or through an outlet structure. The effluent flow rate is approximately equal to the influent flow rate for continuously operating facilities. As the material consolidates pore water (probably contaminated) is squeezed out. Consolidation continues for long periods following disposal, decreasing the volume occupied. After disposal has stopped and water has been decanted from the facility, the surface begins to dry. This aids further consolidation. Most CDFs receive material periodically over a long time.

Due to the increasing difficulty in allocating dredged material placement sites beneficial use of the sites, once placement operations have been completed, becomes an indispensable element of many placement projects. Numerous examples can be found in the literature both for water-based and land-based CDFs, including for instance, habitat development and landscaping.

Environmental concerns associated with CDFs include potential direct physical impacts and contaminant impacts. Others, such as noise, air pollution, aesthetics, cultural resources, etc. and impacts on the health of the operating crew must be properly addressed but are beyond the scope of this report.

The Netherlands Slufter Scheme is an example of a CDF that has been designed to store the contaminated sediments from the Port of Rotterdam until such time as the technology has been developed which will render the material harmless at an affordable cost.

1.5.4 Encapsulation

Encapsulation is an innovative technology for injecting contaminated silty material into a layer of clean silt (i.e. particles less than 0.06mm). Many contaminants are absorbed by fine fraction of silt, thus silt has the capacity to immobilise and render harmless many toxic elements (Davids et al 1992). This is a valuable property of the fine fraction of the sedimented material. Adsorption is a reversible process which is influenced by aerobic or anaerobic environment, acidity and redox potential. Adsorbed substances can only be transported by erosion or through uptake by biological life. As long as the chemical equilibrium is not disturbed the contaminants will remain entrapped in the soil. Since many silts exhibit characteristics of a Bingham body (pseudo-plastic behaviour), the contaminated silt body will remain intact as if it were a solid body.

Before encapsulation is contemplated the rheological properties of the silt layer must be known. If a large enough silt layer is not available a pit or depression may be excavated and filled with clean silt of desirable characteristics. Dredgers may be employed to pump the contaminated material from the site directly into a silt layer for encapsulation.

1.6 Treatment

This report investigates the treatment technologies that are already available and assesses their applicability. It also investigates new technologies and identifies those that have the potential for further development.

It is only relatively recently that treatment of contaminated sediments has been a serious option. It has never before been considered economically viable. However, the changes in legislation controlling disposal at sea and on land and the principles of sustainability have created a different economic climate. For example New York/ New Jersey Port, faced with the alternative of closure of the port (or severe limitation on vessel size) has recently set aside $130million to attempt to find a solution to the treatment and disposal of harbour sediments. The problem is scale. Technologies exist to deal with most contaminants but many are only conceivable at laboratory scale.

Treatment is defined as a way of processing contaminated dredged material (CDM) with the aim of reducing the amount of contaminated material or reducing the contamination to meet specified targets or regulatory standards and guidelines. There is no single "cure all" technology and each sediment requires proper analysis, assessment and prescription for treatment. This may involve more than one treatment process to deal with a range of contaminants in varying proportions. The technologies are described and discussed in detail in Chapter 3.

Treatment may take place in situ or ex situ. In-situ treatments include solidification/stabilisation, biological treatment, chemical treatment and ground freezing. These techniques eliminate the need for removal of contaminated sediments and are best suited for shallow, low energy sites. A brief introduction to the various options is given here.

1.6.1 In-situ solidification/stabilisation

This technique involves immobilising the contaminants by treating the sediments with reagents to solidify or fix them (USEPA 1993). The solidifying reagent binds the pollutants to reduce their transfer to water and biota. There are several factors that should be considered before this technique is selected:

- The need for future dredging or construction at the site;
- The accuracy with which the reagent can be applied;
- Practical limitations such as water depth and accessibility.

1.6.2 In-situ biological treatment

This technique involves biological degradation of the contaminants by controlling organic concentrations, amount of oxygen, amount of nutrients and temperature (Jafvert and Rogers 1991). This can be achieved in two ways:

- Aerobic treatment, which uses aerobic organisms in an oxygen and nutrient rich environment;
- Anaerobic treatment, which uses organisms that survive in an oxygen-deficient environment.

Anaerobic treatment is slower than aerobic treatment and applies only to a few compounds. More studies are needed to characterise the natural bio-degradation of contaminants in an aquatic environment.

1.6.3 In-situ chemical treatment

This involves using chemical agents to change the nature of contaminants by techniques such as neutralisation, precipitation, oxidation, and chemical de-chlorination (USEPA 1993). These techniques have the potential for secondary impacts due to toxic treatment reagents and potentially toxic degradation products. Their application is therefore recommended only for shallow water areas where the site can be hydraulically isolated and de-watered.

1.6.4 Ground freezing

Ground freezing involves placing refrigerating probes in the sediments at close intervals and cooling them from a portable refrigeration unit (USEPA 1985). The resulting ice crystals form a wall of frozen sediment, which is then removed. The process is extremely slow and requires high energy input. It is recommended only for shallow water areas with small volumes of contaminated sediments.

1.6.5 In-situ electro-kinetic treatment

In this method a constant DC current applied to a saturated soil containing contaminants will lead to metal ions and other cations collecting at the cathode whilst anions head towards the positive anode. There are four mechanisms of ion transport, electro-osmotic advection, advection under hydraulic potential differences, diffusion due to concentration gradients and ion migration as a consequence of electrical gradient. The method has the attractive potential to be used in situ to remove heavy metal contaminants, thus avoiding the need for special handling and containment.

A number of firms offer this technique for land remediation. It is relatively untried for river or estuarine sediments. The main difference is the amount of moisture present in the sediment. Pilot scale tests are in progress in the UK attempting to remove very high concentrations of mercury from canal sediments. The choice of material for the electrodes is important as the process removes a number of other elements in addition to the target metal depending on their relative position in the periodic table. A field experiment is reported in Appendix 1.

1.6.6 Ex-situ treatment

Ex-situ treatment ranges from separation techniques (separating contaminated mud from relatively clean sand) to incineration. Some techniques are well developed but others are still in the early stages of development.

Treatment processes may be classed as follows:
- Pre-treatment (dewatering and physical separation);
- Thermal destruction;
- Thermal desorption;
- Immobilisation
- Extraction
- Chemical treatment
- Bioremediation
- Electrokinetic
- Natural ripening

1.7 Treating contaminated sediment instead of soil

A number of technologies are already used for soil remediation that may have application to sediment treatment. The science of contaminated land and soil clean-up is more advanced than that of sediment clean-up and there are a large number of studies, bench and pilot scale related to soils. A relatively large number of remediation projects have been undertaken full scale. There are a number of differences that affect the development and use of decontamination technologies for sediment. Firstly, the market forces and funding are different. Secondly, on a more technical level, the physical and chemical properties are different which will effect the handling and the efficacy of a decontamination technology.

1.7.1 Market forces and funding

It is known that for the development of decontamination technologies there needs to be a market or need for their use. For both soils and sediments a lot of technologies are in their infancy. However, the legislative, regulatory and other forces governing the requirement, demand and use of decontamination technologies for sediment are different from those of soils. Also the logistics of assessing, monitoring and implementing projects. For contaminated land when a site has been cleaned up there is a more obvious and useable resource- the land, which can then be developed on and will therefore have a measurable market value. For sediments or the aquatic system they are dredged from, this is not usually the case. Typically, less money and funding is available for the development of technologies for sediment clean-up.

1.7.2 Physical and chemical properties

The sediment in the aquatic environment, although derived from soil run-off, differs in several physical and chemical properties. The different physico-chemical conditions and different metal species likely to be present as a result are worth noting. The much greater water content of sediment is important when handling the material and for its role in the mobilisation and transport of contaminants. In addition, the physico-chemical differences between soils and sediments affect both the contaminants and their behaviour in the sediment is vital to the effectiveness of the treatment process. Surrounding physico-chemical conditions will influence processes such as adsorption and desorption of contaminant to and from the sediment particles by shifting the equilibrium process. Sediments are typically anoxic (lacking in oxygen), thus the occurrence of metals in a reduced form is likely. In addition, some metals and organic contaminants may form complexes with organic ligands. The type and properties of the organic matter present in sediments differ from that in soils. Sediments typically display much larger concentrations of organic matter compared with soils, because of vegetation, detritus and aquatic life.

As different soil and sediment types vary considerably in their concentrations of the contaminants to be removed as well as constituents such as organic and inorganic material, laboratory studies are needed to assess whether treatment technologies are suitable for a particular contaminant and soil or sediment type. Relevant data needed from the laboratory assessment are details of sample preparation, analytical results and variance in data, conditioning chemicals added (if any) and data on the treatment process. For some technologies, the rate of decrease in concentration of the contaminants in relation to the amount of energy or solvent used is of significance to the evaluation of the effectiveness of the method in treating contaminants.

1.8 Research programmes in other countries

The absence of a country from this section does not imply that no research is being carried out in that country, indeed many countries are involved in the search for solutions to the contaminated dredged material problem. The reason for including those mentioned is that information has been made available concerning substantial national programmes of research. The literature review carried out in the context of this report has been on a world-wide basis.

1.8.1 USA and Canada

Research or demonstration programmes focusing on treatment of contaminated material have been established in a number of countries to varying extents. Environment Canada's Contaminated Sediment Treatment Technology Program (CSTTP), Quebec Development and Demonstration of Site Remediation Technologies program (DESRT) and the U.S. Environmental Protection Agency's (USEPA) Assessment and Remediation of Contaminated Sediments (ARCS) program are both concerned with problems of the Great Lakes. In addition, sediment decontamination demonstrations for contaminated sediment from the New York/ New Jersey Harbour are reported in the literature. Additional information and experience of treatment technologies is available from the USEPA's Superfund Innovative Technology Evaluation (SITE) Program and the site-specific investigations.

1.8.2 The Netherlands

The Development Program Treatment Processes (DPTP) (Dutch abbreviation POSW) in the Netherlands has been actively investigating treatment technologies for sediments and has been running for many years (DPTP 1992 and Ferdinandy 1996). From 1989 to 1997 the Dutch Ministry of Transport, Public Works and Water Management carried out a research and development programme for dredging and remediation of contaminated sediments. The goal of this research was to develop environmentally and economically sound remediation techniques for polluted sediments that will be operational at real-life scale. The organisation of the POSW was the responsiblity of RIZA (Institute for Inland Water Management and Waste Water Treatment). It concerned 50 projects carried out by universities, consulting engineers, contractors and research centres. In the first phase (1989 – 1991) a large number of mainly laboratory, feasibility and desk studies were carried out. In later years the promising ones were scaled up to plant scale. Breakthroughs in treatment efficiency, particularly in biological processes, are occurring rapidly. The Netherlands organisation for applied Scientific Research (TNO) has been carrying out research programmes since the 1980's.

1.8.3 France

Boutouil and Levacher (1997) report studies examining solidification and stabilisation of contaminated dredged material using different types of cement, lime and polymer (Le Gouevec 1996). The studies are a part of a research programme conducted by Le Laboratoire de Mecanique – Groupe de Recherche en Genie Civil which includes characterisation, treatment of contaminants (Marot 1995), treatment by solidification/stabilisation and consolidation.

2. CONTAMINANTS – ORIGINS, CONCERNS AND STANDARDS

2.1 Background

2.1.1 Sources and inputs

Contaminants are substances in the environment that occur above expected background concentrations through their introduction by man or due to geochemical extremes. A contaminant subsequently becomes a pollutant when it reaches concentrations that cause a biological effect. Some naturally occurring elements, such as several trace metals (e.g. Cu, Zn) are essential and `beneficial' at certain concentrations. With increasing concentrations, metals may become inhibitory and ultimately toxic. Compounds, such as organic contaminants, are man-made and at sufficiently high concentrations their presence can be deleterious.

Contaminants may enter sediment systems from a variety of sources and by many different routes. Estuaries that are heavily used by shipping have been shown to contain concentrations of metals 500 times greater than those sediments from the least contaminated estuaries and ports (Murray and Norton, 1979).

A wide suite of contaminants may be expected to be present at any one location from both historical and contemporary discharges which have led to the accumulation of contaminants in sediment, water and biota compartments. Contaminated sediments are of concern when dredging operations are to be undertaken and can subsequently cause a disposal problem if they are contaminated to the extent where traditional sea disposal is now restricted due to more stringent regulations. Contaminants generally recognised to be of concern in estuarine environments include metals (such as Hg, Pb, Cu, Cd and Zn), organobutyl tin (e.g. tributyltin (TBT)), organochlorinated pesticides (OCLs), organophosphorus insecticides (OPs), polychlorinated biphenyls (PCBs), herbicides, oil products, polyaromatic hydrocarbons (PAH's), dioxins and furans. The extent of contamination within dredged material will vary greatly. Currently, in the U.K. on-going research studies monitor contaminants such as metals, OCLs, PCBs and oil products. However, other contaminants which are less routinely determined include herbicides, PAH's, dioxins and furans. These may well be of as yet unrecognised importance. Contaminants may concentrate up the food chain (biomagnification) increasing the exposure and threat to higher organisms. Bryan (1984) suggests that mercury, and more specifically methyl mercury, is the only metal for which evidence exists for biomagnification up marine food chains. However, organic contaminants, such as organochlorine pesticides (OCLs), PCBs and TBT also have the ability to bioaccumulate and biomagnify, are ubiquitous and persistent compounds in the environment and despite restrictions and even bans on their use, are still of concern today.

Contemporary contaminant inputs include numerous and heavily applied agrochemicals which may be discharged into estuarine and coastal areas either directly, via sluice exits, may be transported from inland catchments by rivers or, of recently recognised importance, reach estuarine areas by atmospheric deposition. Seasonal herbicide use results in potentially high transient inputs of herbicides into estuarine areas. Changes in the social and economic climate and administrative and institutional systems can influence the type and concentration of contaminants within the estuarine environment. In the UK and many other developed countries inputs to the aquatic environment have been reduced and water quality improved through legislative restrictions (e.g. U.K. legislation, EC Directives and international conventions), improved wastewater and effluent treatment processes and controls over use. Legislation of current importance controlling contaminant inputs to estuaries includes the Urban Waste Water Directive (DIR 91/271/EEC), which states that secondary treatment of waste is to be a minimum requirement before discharge to certain estuarine areas; member states must comply by 31st December, 2000.

The impact of a more widespread secondary treatment of waste waters, prior to discharge, should reduce contaminant inputs and improve water quality with respect to organic matter and some contaminants, but nutrients and herbicides will not necessarily be strongly affected. While many contaminants will be permanently reduced during secondary treatment, others will be removed and concentrated into sludges to be further treated or disposed of. The distinction is not necessarily relevant as regards direct inputs to estuaries, but is important if an integrated approach to the pollution of the environment as a whole is to be considered. As these point sources to estuarine environments are controlled, diffuse sources to estuarine areas, such as pesticides from agricultural activities and other contaminants, may become the focus of attention in the future.

The main international convention for the reception of waste from ships in ports, MARPOL regulates the types and quantities of waste ships can discharge to sea and continues to reduce contaminant inputs to the sea. Improved methods in oil spill control have helped to minimise the spread and impact of contaminants, such as hydrocarbons. Generally, in the U.K. estuarine sediments are generally expected to get less contaminated with time as point sources are reduced and water quality improved.

2.1.2 Transfer and release of contaminants by sediments

Contaminants may become strongly associated with sediments. Their exchange and distribution will depend on the surrounding physico-chemical parameters.

2.1.3 Toxic effects of contaminants and survival of estuarine biota

The importance of biological activity in estuaries to sediment stability and morphological processes has been identified earlier. Studies investigating the effects of contaminants and pollutants on salt water organisms have been periodically reviewed (Reisch *et al.*, 1981, 1984, 1988, 1991). The immediate effects of contaminants are on individual organisms, by either direct toxicity or altering the surrounding environment. However, the ecological significance of pollutants on the estuarine system is determined by their indirect impact on the populations of species. Assessing actual impacts of contaminants in estuarine environments at an ecosystem level is hindered by a lack of specific and meaningful data, the dynamic nature of estuaries and the undetermined interactions. Most toxicological data is based on acute (LD50) tests with contaminants at high concentrations. LD 50 is the dose that is required to kill 50% of organisms in a given time, a useful measure for bacteria or water fleas but not very applicable to humans!

Chronic effects of different concentrations of contaminants are understudied. The extrapolation of laboratory data to the field, where a host of undetermined biological, chemical and physical processes are occurring, is often not meaningful. For example, the additive or synergistic effects of a suite of contaminants alongside both natural and other anthropogenic stresses are unknown.

The environmental toxicities of mixtures of contaminants to estuarine/marine organisms are complex. Some compounds are known to be toxic. TBT is a very toxic biocide intentionally introduced into the aquatic environment for use as an anti-fouling agent and, as a consequence of its use, there is a widespread occurrence of TBT in European estuaries and marinas. The biological effects of TBT on non-target organisms (e.g. bivalves and molluscs) have been recognised at lower concentrations than was ever envisaged and declines in bivalve populations observed (Langston *et al.*, 1987).

In order to assess the degree of treatment required, or its effectiveness, it is necessary to have some knowledge of the relevant contaminant concentrations. Toxic simply means "too much". Highly toxic substances may be fatal to man after an intake of say 1mg while a similar quantity of common toxic substances such as table salt and alcohol would have a negligible effect. In the following sections the main groups of environmental contaminants are reviewed.

2.1.4 Global distribution of contaminants

A Global Waste Survey was initiated by the London Convention in 1991 for the purpose of addressing the potential implications of the ban on ocean dumping of industrial waste on countries worldwide, especially in developing countries, and to formulate a plan that would assist Contracting Parties to address their commitment to technical assistance and capacity building in a practical and cost-effective manner (IMO 1995).

The most frequently acknowledged waste types are hospital wastes, waste oils, heavy metals and inorganic chemicals and sludges and acids/alkalis. The lowest percentages are for PCB's and contaminated soils . This may be due to the fact that PCB use in electrical transformers and capacitors was either not universal, or that such equipment has already been removed. [PCB's from transformers was the particular problem at Blyth, see Appendix 3]. The problem of soil contamination is less prevalent and less recognisable in countries with a relatively short industrial history.

Hazardous waste generation is reported in the National Profiles of 13 countries (IMO 1995). The data has been categorised under three generic headings in Table 2.1, namely:

- Organic/oily wastes;
- Inorganic wastes;
- Miscellaneous/sludge wastes.

Table 2.1 Estimated quantities of hazardous waste (thousands of tonnes/year)

Country	Organic/Oily Wastes	Inorganic Wastes	Miscellaneous Waste and Sludges	Totals
OECD				
Canada	2196	3930	376	6502
Germany	1117	2353	2468	5936
Ireland	48	7	12	67
Netherlands	298	31	489	818
Middle East/Africa				
Bahrain	23	1	71	95
Egypt	4	15	43	63
Nigeria	58	*	49	107
Latin American/ Caribbean				
Chile	*	*	*	*
Mexico	*	*	*	5292
Trinidad and Tobago	32	2	18	52
Eastern Europe				
Hungary	685	720	602	2007
Poland	*	*	*	1300
Romania	*	*	*	*
Asia/Pacific				
China	800	10100	36100	47000
Fiji	*	*	*	*
Philippines	17	25000	6	25023
Thailand	316	41	562	919

Variations in the relative composition of hazardous waste among the regions are largely indicative of dominant industries in each region. For example, in Middle East and Africa, large quantities of miscellaneous waste and sludges and organic and oily waste arise from the mining and metallurgical sector and the petroleum industry in the region.

The miscellaneous/sludges category for the Asia Pacific region is dominated by the metallurgical sector and metallic sludges, while in Eastern Europe the category is primarily an indication of sludges produced as by-products from manufacturing and wastewater treatment processes. The OECD miscellaneous/sludges category is comprised no only of process sludges, but also miscellaneous wastes such as contaminated soils, collected dust and fibres from manufacturing processes, hospital wastes and post-consumer products such as batteries.

The high proportion of inorganic waste arisings in three of the regions typically refers to acids and alkalis, often associated with secondary industries, such as metal finishing, electronics and manufacturing. Again for OECD countries, Eastern Asia/Pacific regions, this is a fairly accurate reflection of the relative contribution of the manufacturing sector to the GDP of each region.

2.1.5 General classification

A number of classifications for contaminants are possible. The one that has been adopted for this report is as follows:

Inorganic contaminants:
- Metals
- Nutrients

Organo-metallic contaminants
- TBT's
- Methyl Mercury

Organic contaminants
- Chlorinated organics
    - Organo chlorinated pesticides (OCH's)
    - PCB's
    - Dioxins and Furans
- Non-chlorinated organics
    - Hydrocarbons, oil and oil products
    - PAH's
- Endocrine disrupters

2.2 Inorganic contaminants

2.2.1 Heavy metals

2.2.1.1 General introduction

Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc are all classified as heavy metals. Of these cadmium and mercury appear in the London Convention's original Annex I (list of prohibited substances for dumping), arsenic, lead, copper, zinc, chromium and nickel are in Annex II (substances requiring special care). Copper and zinc are essential trace elements in the nutrition of organisms, so concentrations that are too low are harmful to an ecosystem. These toxic metals are widely used by man and most inshore seabeds have enhanced concentrations. Several accidents are reported in the literature. The most famous one being the Minamata accident in Japan where organo-mercury compounds had serious effects on the population through the ingestion of contaminated fish (in Donze et al 1990).

There is little knowledge of the level at which the various metals become harmful, which is why there is a lack of absolute standards. The long term effects are extremely difficult to measure. For example some metals may have carcinogenic and mutagenetic properties. In recent research it has been found that it is not just the metal but the specific form of the compound that influences the toxic effect on the organism. This means it is extremely difficult to set standards and is the fundamental reason for the establishment of the "precautionary approach" adopted by the international conventions by virtue of which “preventative measures are to be taken when there are reasonable grounds for concern that substances or energy introduced into the marine environment may bring about hazard, harm, damage or interference, even when there is no conclusive evidence of a causal relationship between inputs and the effects".

Metal concentrations of the sediments depend on the metal input to the water and the environmental conditions. The latter determines the dissolved and adsorbed fractions in the water. Due to increasing salinity and decreasing oxygen and pH, desorption of metal takes place, causing an increase in the dissolved fraction. On the other hand, flocculation will take place due to increasing chlorine content, which will cause adsorption of metals onto the sediment and deposition of the flocculated particles.

Once the sediment particles have settled, many kinds of processes take place. Different chemical bonds affect the biological availability and therefore the toxicity. The forms in which heavy metals may occur are listed in order of increasing strength of retention (Kliem et al 1997):

1. Soluble
2. Exchangeable
3. Specifically adsorbed;
4. Adsorbed on insoluble organic material
5. Adsorbed on, or occluded in, oxides of iron, aluminium or manganese;
6. As constituents of primary minerals (crystal lattice).

Soluble heavy metals are found in the material solution as ions or as soluble complexes with inorganic or organic ligands.

Exchangeable heavy metals are predominantly held by electrostatic forces on negatively charged sites on clays, other minerals or organic material. The distinction between ionic and covalently binding of cations is not sharp; some cations may be taken up rapidly by ionic forces and then pass over slowly to a covalent or coordinate combination (Becket 1989) as seen in the group of specifically adsorbed heavy metals.

The specifically adsorbed metals have a stronger retention because the heavy metal ions fit to the specific site on the soil particle.

In organic material heavy metal cations are mainly complexed or chelated by organic matter.

Iron, aluminium and manganese are all common elements in dredged material. The oxides and hydroxides of these are rarely pure. They usually contain cations from each other and heavy metal cations as well. Heavy metal cations are easily adsorbed on such solids, especially when the host solid is amorphous. Initially the adsorbed heavy metal will be held in exchangeable form but the binding may change to more specifically covalent with time (Becket 1989). In general the surface of hydrous iron and manganese oxides are strong scavenging agents for heavy metals (Chao 1972). Their capacity to adsorb heavy metal cations from the solution is controlled by pH and crystallinity. As the oxides crystallise the adsorbed cations may become included in the crystal structure or they may be expelled to the still amorphous surface layers.

In some minerals the heavy metals are found in the crystal lattice. New precipitates of carbonates, sulphides, phosphates, hydroxides etc may be newly formed compounds of the heavy metals themselves. If so, they may contain more than one heavy metal, and often form mixed crystals with the corresponding compound of major elements, usually calcium or iron. Minor amounts of heavy metal cations may be incorporated in new precipitates of compounds of calcium, magnesium, iron or aluminium as they form, or may be adsorbed on the amorphous surface of such precipitates.

In order to establish the forms in which the heavy metal exists in a particular instance an extraction procedure is used. The ease of release of occluded heavy metal cations is expected to depend on the solubility of the mineral in which they are held. Thus an extractant that dissolves a particular group or iron oxide etc also mobilises the heavy metals that it contains. In general 3 – 8 extractants are used in sequence. The first are the least aggressive and most specific. Subsequent extractants are more aggressive and less specific.

Aquatic organisms will concentrate metals from the ambient water to levels far exceeding the metal levels in the water, thus retaining them within the biologically active coastal waters. High standing crops of phyto- and zooplankton may absorb a large part of the metals brought to the coastal zone via rivers and outfalls. Included into faecal pellets or dead organisms, the metals may then settle and become incorporated into coastal sediments.

Many metals are released into the environment in relatively non-toxic forms. Subsequently they may acquire an enhanced toxicity as organometallic compounds, through environmental interactions involving both biological and non-biological processes.

Donze et al (1990) provide a useful description of the occurrence and concerns regarding heavy metals.

2.2.1.2 Arsenic

Arsenic usually exists in nature in sulphide ores. The major uses of arsenic currently are in pesticides, herbicides, cotton desiccants and wood preservatives. Arsenic also serves as a bronzing or decolourising agent in the manufacture of glass, especially opal glass, and enamels. Historically it has been used in dyestuffs and chemical warfare gases and it is still used in the purification of industrial gases for the removal of sulphur.

2.2.1.3 Cadmium

Cadmium production is linked to primary zinc production, since cadmium is a component of the zinc ore. Its main uses are in nickel/cadmium batteries, as bright yellow pigments in paints and as a stabiliser of synthetic material. It can indirectly be released as part of phosphate feeds and fertilizers.

Cadmium is present in iron ore and fossil fuels, which also lead to emissions, for example, during the burning of petroleum.

Cadmium is a black list substance in an EC Guideline 1976 and in the old Annex 1 of the London Convention 1972.

2.2.1.4 Chromium

Chromium is one of the least toxic of the trace elements on the basis of its oversupply and essentiality. Generally the body of animals can tolerate 100 to 200 times its total body content of chromium without harmful effects. The principal industrial consumers of chromium are the metallurgical, refractory and chemical industries. An important consumer for many years has been the tanning industry. Other uses are in pigment production and industries using chromium alloy for plated materials.

2.2.1.5 Copper

Copper is unusual in that it is usually used in its pure state because of its excellent conductivity of electricity and heat. It is also used in its alloys like brass and bronze. Copper will usually precipitate from the water phase and as a result concentrations in sediments may become high. About 1% of dissolved copper is regarded as unstable and as a result is biologically easily available. A high proportion is usually associated with sediment.

About 1% of the dissolved copper is regarded as unstable and, as a result, biologically easily accessible. It is estimated that 0.01 to 0.1% of the total copper occurs as free hydrated cation, 1 – 10% as a complex combined with dissolved and colloidal organic matter and 25-90% associated with suspended particles.

Copper is accumulated to a high level by a number of organisms at various trophic levels. Based on BCF values of about 1000 and the persistence of copper, a high level of accumulation may be expected in the aquatic environment, especially in invertebrates. Fish do not accumulate very much copper.

2.2.1.6 Lead

Lead minerals are galena (lead sulphide), cerrusite (lead carbonate) and anglesite (lead sulphate). Galena occurs mainly in deposits that also contain zinc minerals and small amounts of copper, iron and a variety of trace elements. Mixed lead and zinc ores account for about 70% of total primary lead production. Lead is also produced from scrap (secondary lead) which accounts for about 35% of the total world supply of lead. Total production (primary and secondary) amounts to about 5 million tonnes/year.

Lead is mainly used in storage batteries (40%) alkyl lead production (12%), cable sheathing (9.2%), pigments(12%), alloys (10.8%). Lead is poorly soluble in water and accumulates in the food chain as a cumulative poison.

2.2.1.7 Mercury

Mercury exists in the earth's crust mainly in the form of various sulphides. The world production in 1973 was about 10,000 tonnes/year. Another 10,00 tonnes is released into the environment through human activities such as the combustion of fossil fuels and waste disposal. These figures should be compared with natural release through degassing from the earth's crust and the oceans, estimated between 30,000 and 150,000 tonnes/year. Organic mercury compounds released into the environment may persist but can be broken down to elemental mercury or mercuric compounds.

About 25% is consumed by the chlor-alkali industry, 20% is used in electrical equipment, 15% in paint, 10% in measurement and control systems such as thermometers, 5% in agriculture, 3% in dental practice and 2% in laboratories. The cytoxic properties of mercury compounds have led to a widespread usage as germicides and fungicides. Most industrial countries have now banned this use and the alkyl-mercury compounds have decreased. This trace metal is considered non-essential and highly toxic for living organisms. Even at low concentrations mercury and its compounds present potential hazards due to enrichment in the food chain.

2.2.1.8 Nickel

Nickel is found in sulphide ores, mainly those mined underground, and in oxide ores which are mined in open pits. Nickel is also produced by the carbonyl process, whereby nickel carbonyl is formed then heated so that it decomposes into high purity nickel and carbon monoxide. In 1973 the world production was about 660,000 tonnes.

About 40% of nickel produced is used in steel production. It is also used in other alloys for coins and various household utensils. Electroplating with nickel sulphate accounts for a further 20%. Nickel hydroxide is used in nickel-cadmium batteries. Nickel is considered to be essential for several animal species but its necessity for human beings has not yet been shown.

2.2.1.9 Zinc

Worldwide production in 1987 was estimated at 5 million tonnes of which 2 million tonnes was in Europe.

The most important uses of zinc are protection against corrosion, leaf-zinc in roof guttering, in alloys with copper (brass) , components of injection moulding alloys in cars, washing machines, etc., batteries, as an oxide in rubber tyres, as organic zinc in as "dope" in oils and an additive in animal feed stuffs. Zinc is one of the most abundant, essential trace elements in the human body. It is a constituent of all cells and several enzymes depend upon it as a cofactor. Accumulation in the food chain does not seem to be of importance.

2.2.2 Nutrients

2.2.2.1 Nitrates

Increased concentrations of nutrients (N and P) from sediments to surface waters or water courses may lead to increased plant growth and to nuisance blooms of algae. Typically, nutrient concentrations may be high in contaminated sediments. The removal of nutrients may be desirable for some sediments. In addition, nutrients will enhance bioremediation processes and are important for treatment and microbially breaking down organic contaminants. In some circumstances the addition of nutrients to sediments may be desirable. The implications of nutrients in sediments therefore depends on the nutrient concentrations, sediment, surrounding environment and other contaminants present.

Nitrogen can be present in many forms and the availability of the nitrogen to the biota is of importance. Most algae can use ammonical nitrogen, nitrite and nitrate while some use ammonical nitrogen preferentially. Nitrogen in the nitrate form is found in chemical and natural fertilizers, as well as in sewage.

2.2.2.2 Phosphates

Phosphates are critical components in life processes. They have unique properties that are valued in many industrial and food grade applications. Animal feed lots, dairies and wastewater treatment plants can add phosphorus to streams. Phosphates exist in many forms, orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Phosphates can cause eutrophication of lakes and rivers by stimulating growth of algae and upsetting the natural balance. In general, algal productivity of lakes increases with increasing concentrations of P rather than N. The phosphate crystal lattice carries a negative charge, which is balanced by positive sodium ions (cations) in the interstices.

2.3 Organo-metallic contaminants

2.3.1 TBT

Tributyltin (TBT) is an organo-tin compound used as a biocide in antifouling paint on ship hulls. It usually enters into the aquatic environment by leaching from the ship hulls or as wastewater discharging from dock yards or marinas. The contaminant loads in sediments depend on shipping activity in the area and the leaching rate of TBT formulas. The concern about its presence in the aquatic environment arises as it has been shown to be harmful to non-target organisms and has consequently been banned in some parts of the world from use on boats of less than 25m in length. More recently there is a call for a total ban on its use.

2.3.2 Methyl mercury

Methyl mercury is toxic to man. Poisoning by methyl-mercury compounds presents a bizarre neurological picture, as observed in the large-scale outbreaks in Japan and Iraq.

Methyl-mercury may be discharged directly to the environment but is naturally formed in the aquatic and terrestrial environment form elemental mercury and mercuric mercury. This methylation reaction is likely to occur in the upper sedimentary layers of the aquatic systems. The methyl-mercury formed may be taken up by living organisms and accumulate in the aquatic environment. Some methyl-mercury may also be released into the air. The local load of methylated mercury may be considerably increased by industrial release of mercuric compounds. This has been shown for mercury release from chemical, paper-pulp and alkaline chlorine factories.

2.4 Organic substances

Organic compounds occur naturally, but the majority of them have been synthesised by man. Their fate in the aquatic environment is highly dependent on their sorption onto suspended particulates, particularly the organic matter. PAH's in the environment are generally associated with heavy industrial activity. PCBs. although declining significantly in the UK are still reaching the environment from industrial and municipal sources.

The relative toxicity of the organic substances absorbed onto the river sediments can be judged against figures reported to the London Convention by the Netherlands, of "harmless levels" and "maximum quality" of carcinogenic materials. In the Netherlands, "harmless level" is currently recognised as the "no effect" level. Although referred to a "standard soil" containing 10% organic matter and with 25% less than 2 micron, these appear to be the only figures for the quality of dredging for disposal which are currently applied in Europe and are themselves under review.

2.4.1 Chlorinated organics

Organochlorines are substances containing chemically combined chlorine and carbon. Most are toxic, persistent and tend to bioaccumulate in the environment. These qualities make them arguably the most dangerous group of chemicals to which natural systems can be exposed. Around 11,000 organochlorines have been identified. Very few of these occur naturally; most are produced and released by industry. Synthetic organochlorines result from all industrial processes that produce or use chlorine. They are created either deliberately as a product or by-product, or incidentally after the release of other chlorinated compounds, which then react in the environment to form new and often more toxic organochlorines.

Chlorine production began in 1893 and now exceeds 40 million tonnes per year. Organochlorines are now present in water, in air, in living things everywhere on earth. The north east Atlantic is considered to be the largest reservoir of the group known as PCB's (see 2.4.1.2) in the world (Greenpeace, 1992).

Most organochlorines are extremely stable. As a result they persist in the environment for a very long time. When they do break down the usually produce more hazardous or more persistent forms than the original substance. Since most are not soluble in water they tend to migrate, the more volatile ones (like CFC's) to the water surface and from there to the atmosphere, the less volatile ones (like PCB's) into sediments and from there into the food chain. Organochlorines bioaccumulate because they dissolve in fat and so build up in the fatty tissue of living things. Those that have accumulated in fatty tissue can be transferred via the placenta or breast milk to the next generation, sometimes in high concentrations. It has been estimated that residues passed in this way may still be detectable after 5 generations.

Organochlorines are highly toxic. They act in several ways to interfere with the most fundamental biological processes. They can cause reproductive failure and infertility in females, impair the development of offspring, lead to feminisation and demasulinisation of males, disrupt the immune system, leaving organisms more susceptible to disease, contribute to the development of cancer and damage the nervous system, liver, kidneys and other organs.

2.4.1.1 Organo chlorinated pesticides

It is the main intention of manufactured pesticides that they should be distributed in the environment. A brief review of a number of pesticides is given in the following sections. A standard parameter used is the bio-concentration factor (BCF). This is the concentration found in organisms compared to the same substance dissolved in water. A BCF of 1000 means that organisms can build up a concentration that is 1000 times higher than the concentration found in the aquatic environment.

Aldrin
This substance was developed as an insecticide and it shows strong bio-accumulation and adsorption to solid particles. It is poorly soluble in water and it specifically toxic for insects and also fish. BCF is about 2000.

Dieldrin
Dieldrin is produced in Pernis in the Netherlands. Its use was forbidden by EC Directive from 1981. It is now mainly used for combatting termites in other countries. It is a transformation product of aldrin and it is somewhat less toxic than the parent substance. However its persistence, the risk of high bio-accumulation and its high toxicity for fish means that it is a very dangerous substance especially in the aquatic environment. BCF is about 3000.

Endrin
This is a moderately poisonous substance, especially for warm-blooded organisms. It is somewhat less toxic for fish. It is resistant to bio-degradation. It is forbidden by the same EC Directive as Dieldrin. BCF is about 3000.

DDT and Derivates
DDT and its products which arise from transformation and decomposition (DDD and DDE) are substances that should be kept out of surface water because they are persistent and highly toxic to fish. DDT is still produced in Europe in quite large amounts in Spain, Italy and France.

The transformation reactions may occur in living organisms and then be released to the surrounding water. Degradation reactions also occur at high temperatures or during careless storage. Although banned for use and sale under the EC Directive from 1981 it is still used in tropical countries for malaria control. BCF ranges from 4600 to 43000.

Endosulphane and sulphate
This is produced in Germany and it is extremely toxic for fish. The alpha-isomer is the more toxic. Endosulphane consists of two isomers: 64-67% alpha-endosulphane and 29-32%beta-sulphane. It is used as an insecticide on all kinds of agricultural and horticultural products. BCF is about 1500.

Heptachlor and Epoxide
Considering the persistence and level of toxicity to fish and the fact that one if its transformation products, heptachlorepoxide, is also very persistent, heptachlor deserve a great deal of attention. It is bio-degraded only very slowly. It is no longer produced in Western Europe and is in decline worldwide. BCF is about 15000.

Chlordan
Chlordan consists of two isomers, cis- and trans-chlordan. Chlordan is very persistent both chemically and biologically and therefore is very undesirable as an aquatic pollutant. It has a high toxicity for fish. It is no longer produced or used. BCF is about 5000.

Hexachlorobutadiene
Hexachlorobutadiene (HCB), a manufactured compound, is readily adsorbed by soil particles. In fresh water more is found in solution than in suspension. In estuaries the reverse is true. The strong adsorption of the compound to soil particles is an advantage in the preparation of HCB-free drinking water from surface water by filtration. It is however a disadvantage from an environmental and public health point of view because it can accumulate in sediments and from there into organisms living in these sediments. In this way HCB can enter the food chain, ultimately leading to uptake by man. Its BCF ranges between 144,000 and 270,000. Based on the limiting levels allowed in eels for consumption sediment should contain less than 1mg/kg (ppm) HCB on a dry weight basis.

Hexachlorocyclohexene

Hexachlorocyclohexene (HCH) is an artificial organochloro compound. It exists as 8 different stereo-isomers, of which gamma-isomer, also known as lindane, is the best known and the most frequently used. Lindane is a very effective insecticide. They have been and still are used quite extensively. Sufficient data to quantify risks on the effects and presence of HCH only exist for the alpha-, beta and gamma isomers. As exposure levels to the remaining HCH isomers are lower, the risks are also estimated to be lower. In view of the persistent character and function of HCH it is obvious that these substances cane a certain risk to the aquatic environment. Lindane is a general purpose pesticide, frequently used in seed treatment and in other agricultural and horticultural processes. It is used on playgrounds and sports fields and against external animal parasites.

An insecticide such as lindane must of course be stable for some application in order to meet its objective as an insect killer. The substance is relatively unreactive with respect to heat and daylight but is unstable in an alkaline environment, decomposing into hydrochloric acid and trichlorobenzene. This leads to faster degradation in the usually weakly alkaline sea water.

Degradation of HCH by bacteria and other organisms does occur. Various metabolites have been identified , including pentachlorocyclohexane, tetra- and trichlorobenzene and chlorophenols. Under anaerobic conditions HCH is easily degraded but under aerobic conditions it is not easily biodegraded. Degradation generally proceeds slowly and mainly leads to the formation of other, rather persistent compounds.

In man, lindane is the most acutely toxic of the HCH family. Studies have shown chronic effects on the liver for all tested isomers (alpha, beta, gamma and delta). Beta HCH shows an estrogenic action. Infertility and decline in vitality of young animals has also been found. Carcinogenicity studies show induction of tumours in liver. Mutagenicicty has not been observed.

Alpha HCH

In both fresh and salt water BCFs range between 100 and 1000. Alpha HCH can be considered a moderate accumulator and it is very toxic in short term tests on fish and crustaceans. No effects within solubility boundaries were found for fresh water and salt water algae. Long term effects on salt water organisms have not been demonstrated.

Beta HCH

Beta HCH shows the same BCF values as alpha HCH and it is also a moderate accumulator. Chemically it shows minor toxicity for crustaceans and is moderately toxic for fish. It has and estrogenic effect on male and female fish. No data on salt water species are available. Preliminary results of a study of the aquatic microcosm show that the effects of Beta HCH can be attributed to a defect in the metabolism of the whole community of organisms.

Gamma HCH

Although no firm information is available about the metabolism of gamma HCH in water and soil organisms and birds, it may be assumed that in these species the removal of HCl is important. BCF values in salt and fresh water range from 100 to 1000. The substance is considered to be a moderate accumulator. Gamma HCH is very toxic for crustaceans, amphibians and fish. Algae, protozoa and mollusca are less susceptible, In salt water Gamma HCH is variably toxic for crustaceans, very toxic for fish and slightly toxic for mollusca and annelids.

2.4.1.2 Polychlorinated biphenyls (PCB's)

Sources

PCB's are man made and widely used. Unfortunately, although they have some outstanding properties, they can be dangerous in the environment. Their special properties are:

- Chemically stable;
- Inflammable PCB's can only be completely burned in air above 800^{0}C;
- Hardly any corrosive action;
- Excellent electrical insulators even at high temperatures;
- Good conductors of heat;
- High boiling point and low vapour pressure;
- Low solubility in water;
- High solubility in fats and organic solvents;
- Lasting thermoplasticity;
- Good attachment to smooth surfaces.

Chemically they are a homogeneous group of compounds, comprising biphenyl skeleton where at one or more hydrogen sites chlorine atoms are substituted. Biphenyls consist of two linked benzene rings. There are 10 sites where a chlorine atom can be inserted: 209 varieties of these molecules have been synthesised.

Since they were first manufactured in 1929 about 2 million tonnes have been made. By way of example in 1980 production in European countries was as follows:

• Federal Republic of Germany	7300 tonnes
• France	6500 tonnes
• Italy	1250 tonnes

Spain, Russia and Czechoslovakia also produced unknown amounts.
70% of the total amount produced has been estimated to be still in use or in storage. The rest has entered the environment. As yet only about one or two percent has entered the oceans.

PCB's have been used in both open and closed systems. In open systems they were used as lubricants, softening agents, impregnating agents, to render products less flammable, brake fluids in measuring instruments, additives in printing inks, carbon paper, paints and greases. In closed systems they are used in large electrical transformers and in condensers for electronic circuits.

Persistence

Unlike pesticides such as DDT, PCB's have no direct outdoor applications but they end up there. Generally they are adsorbed quickly by organic matter. In nature they are transported bound in living or dead organic matter. Rates of transport are quickest in the aquatic environment and it is suspected that eventually a much higher proportion will eventually reach the oceans.

PCB's are among the man-made chemicals that are only degrade very slowly. This means they are persistent in nature. Because they are hardly soluble in water and soluble in fats bio-accumulation in aquatic food chains and bio-concentration are pronounced.

Accumulation

Bio-accumulation means that whenever one type of organism eats another species contaminated with PCB's the PCB's are ingested and transported to the fatty tissue. Here they accumulate because degradation and excretion hardly occur. When this organism is eaten by another higher in the food chain even higher concentrations are built up. Top predators of a food chain, like birds of prey and seals are already showing concentrations so high that the toxic effects are thought to be responsible for population decline.

A clear correlation between solubility in fat and the tendency to absorb onto suspended matter has been observed. The correlation with concentration of suspended organic matter is especially high. Persistence and the solubility in fat increase with increasing levels of chlorine substitution in biphenyls, so the level of bio-concentration also increases.

Toxicity
In the Netherlands a massive die-off or cormorants in 1970 was attributed to the presence of toxic levels of PCB's. Concentrations in the liver were higher than the lethal level as found in experiments. Also the decline of seals in the Wadden Sea and German Bight during the 1980's is probably caused by a lower reproduction rate due to poisoning by PCB's.

The toxicity of the different kinds of PCB is very variable, depending on both the molecule and the species. Absorption and evaporation, being of importance in the distribution processes depend solely on physical and chemical properties of the molecule concerned. Accumulation also depends on the biological degradability of the molecule. It is, for example, known from studies that 10% tricholo-biphenyl in small streams is adsorbed onto sediment while 86 to 87% evaporates. Another complication is caused by the fact that PCB mixtures may contain traces of other compounds, like polychlorinated dibenzofurans. Since these substances often are far more toxic than PCB's it is quite possible that toxic effects are sometimes wrongly attributed to PCB's.

There are some specific toxic effects of PCB's reported. With rats it has been proven that as a sub-chronic effect of PCB's liver alterations appear. It has been proven that PCB's can promote the developments of tumours initially caused by other factors. Tumours in stomach and liver especially show this effect. The molecules with a high chlorine content ate not proven to be mutagenic, since 4-chloro-biphenyl has been proved to be mutagenic for Salmonella. PCB's can influence reproduction. OF the animals tested apes and minks are the most susceptible with respect to this parameter. The number and body weight of descendants decreased.

Some PCB's affect the immunological defence system because they can attach to the TODD receptor in the thymus.

Measurement
When the concentration of PCB's in sediments is determined, usually the sample is not fractionated. Because of the close correlation with organic matter, the organic content is usually determined at the same time. Some German and Dutch groups determine the concentration of selected individual PCB's. The concentrations determined are added up and given as the sum of PCB's.

2.4.1.3 Dioxins and Furans

Dioxin is on of the most toxic chemicals known. A report released in 1994 by the US Environmental Protection Agency describes dioxin as a health hazard with no safe level of exposure. Dioxin is a general term that describes a group of hundreds of chemicals that are highly persistent in the environment. The most toxic compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The toxicity of other dioxins and chemicals like PCB's that act like dioxin are measured in relation to TCDD. Dioxin is formed as an unintentional by-product of many industrial processes involving chlorine, such as waste incineration, chemical and pesticide manufacturing and pulp and paper bleaching. Dioxin was the primary constituent of Agent Orange, was found in Love Canal in Niagara Falls, New York, and the reason for evacuations at Times Beach, MO and Seveso, Italy.

It is formed by burning chlorine based chemical compounds with hydrocarbons. 95% comes from incinerators burning chlorinated waste. It is also affiliated with paper mills which use chlorine bleaching in their process and with the production of Polyvinyl Chloride (PVC) plastics.

Two aspects of the environmental behaviour of dioxin-like compounds make them particularly troublesome. First, they are extraordinarily persistent, resisting physical, chemical and biological degradation for decades. As a result, even dilute discharges accumulate in the environment over time, reaching particularly levels in aquatic sediments and in the food chain. Because they are so long lived they can be transported long distances through the atmosphere and they are now distributed on a truly global basis. Inuit natives of Arctic Canada, for instance, have some of the highest body burdens of dioxins, furans and PCBs recorded, due to a diet dependent on fish and marine mammals (Thornton, 1997).

Second, dioxins are highly oil-soluble but insoluble in water so they bioaccumulate in fatty tissues and are magnified in concentration as they move up the food chain. They are very persistent in human tissue: estimated half-lives in humans are typically 5-10 years (EPA, 1994, cited in Thornton 1997).

Dioxins and dioxin-like contaminants have been linked to increases in cancer of various types and reduced sperm count in men worldwide to half what it was 50 years ago.

2.4.2 Non chlorinated organics

2.4.2.1 Hydrocarbons, oil and oil products

Hydrocarbons constitute a very large and important group of organic compounds, for example most products from natural mineral oil are hydrocarbons. They are present in the environment and sediments from oil spillages.

2.4.2.2 Polycyclic aromatic hydrocarbons (PAH's)

Sources

PAH's enter the environment through industrial processes. In contrast to compounds like DDT and polychlorinated biphenyls (PCB's), they are not individually synthesised and used in end products. They are not useful in the way that PCB's and pesticides are.

PAH's are a group of about organic substances built up from two or more benzene rings. Natural synthesis, processing of mineral oil products and incomplete combustion of organic material are the main pathways by which they are formed. Fossil fuels, such as peat, coal and petroleum, are rich in PAH's. In crude and refined mineral oils very complex PAH's occur. Combustion of organic matter at temperatures between 400 and 2000^0C results in the formation of a large number of different PAH's.

Natural sources of PAH's do exist but do not contribute much to pollution compared to anthropogenic sources. They do not occur as separate substances, but always in mixtures. The ration in which individual PAH's are released into the environment may differ greatly from source to source. This profile can be used to identify from filed measurements and quantify the contribution to the overall PAH levels of different sources.

The main source is industries such as aluminium smelting, coke production, uncontrolled combustion of cables, wood preservation and conservation. Other sources include domestic heating and traffic.

Worldwide the quantity of PAH's entering the aquatic environment is estimated at 230,000 tonnes/year, caused mainly by oil pollution, deposition and precipitation. It occurs mainly in areas where industry and population are concentrated such as deltas, estuaries and coastal waters.

They reach surface waters through accidents, discharges, drainage and deposition. Those which enter the atmosphere form combustion processes will also eventually reach the water by direct deposition or by drainage from land. Industrial and urban waste water is rich in PAH's and only a small percentage is removed by sewage treatment.

On account of their low solubility, PAH's are found at extremely low concentrations in water. They are easily adsorbed onto organic particles and consequently their transport is mainly determined by hydrodynamic processes. The solubility is strongly influenced by temperature and their molecular weight, The higher the molecular weight the lower its solubility. They adsorb preferentially to the smallest particles. They are very soluble in fats and oils.

When suspended matter is brought into contact with water in which PAH's are dissolved 50% of these compounds will be adsorbed within a few hours although 100% can take months. In estuaries the highest concentrations are generally found in the turbidity maximum (or dilution) zone, the area where sedimentation and re-suspension takes place. More than half the load entering a system will eventually be stored in the sediments.

Evaporation transformation and degradation

The concentration may decrease by evaporation and transformation. Evaporation plays a significant role in surface waters and depends on temperature, movement of the water, wind and the molecular weight of the individual substance. Especially with naphthalene and the PAH's containing three rings, evaporation is an important source of loss to the atmosphere (see the "natural recovery" option in Section 1.5.1, however in this case it simply returns the PAH's to the atmosphere and is not an overall solution).

The most important abiotic transformation process for PAH's is photochemical degradation, which is proportional to the content of dissolved oxygen, It might be accelerated by humic acids and increase exponentially with temperature. Large mutal differences in photochemical reactivity exist between the various individual molecules: naphthalene is not highly reactive whereas benzo(a)pyrene is very reactive.

Biological degradation occurs under aerobic conditions and, in sediments, depends strongly upon pH and rH. In undisturbed anaerobic sediment PAH's are virtually stable. The time needed to degrade by bacteria half of the amount of the substances present is inversely proportional to the solubility of the substances in water. Depending on environmental circumstances, the half life for naphthalene ranges between 30,000 and 500,000 hours. Low molecular weight PAH's can be totally degraded in nature into carbon dioxide and water. Larger molecules will be degraded into phenols and acidic metabolites. In addition to these abiotic processes various bacteria are also capable of transforming various PAH's.

Accumulation

Accumulation in the aquatic environment largely depends on the physical and chemical properties of the substance and the exposed species: accumulation and excretion rates are, in general, lower when the molecular weight is higher. The highest rates are found within shell fish and fish. The rate of excretion by these organisms probably upon their ability to metabolise these substances. It is generally found that PAH's, with the exception of naphthalene accumulate in large quantities. The concentration found in organisms are always lower than the levels in surrounding sediment, even for organisms that get their food directly from these sediments. This suggests that PAH's attached to sediments have a lower bio-availability.

Toxicity

For several individual PAH molecules a certain amount of phototoxicity has been demonstrated, resulting in an increase in their toxicity in the presence of light.

Some PAH's are seen as one possible cause of the development of tumours in aquatic organisms. In some studies a correlation between the presence of these substances and alteration in the chromosomes of various freshwater and saltwater organisms has been found. For example a field study in fresh water comparing data from polluted areas (total PAH 18-70 ppm) to data gathered in two unpolluted areas (total PAH 0-17 ppm) showed an increased frequency of tumours in the intestines of fish. The acute toxicity of PAH's for aquatic organisms ranges between about 0.2 and 10ppm. Sub-lethal effects have been reported for concentration between 5 and 100 ppb. In these cases the functions of cell and nuclear membranes are often found to be disturbed.

With respect to humans it is known that naphthalene and anthrcene (PAH's with two and three benzene rings) are not carcinogenic. Other PAH's are definitely carcinogenic, such as benz(a)anthracite, benzo(k)fluoranthene, benzo(a)pyrene, indeno (1,2,3-cd)pyrene and chrysene.

Measurement

The correlation with organic matter is often the reason for measuring organic carbon in the same sample. PAH is usually determined on a total sample, without fractionation. There is some confusion about the parameter "total PAH". Some countries explicitly state which individual PAH levels are to be used to determine the total, others do not state which they use. As there are more than 100 species the value "total PAH" can be misleading. The parameter PAH Borneff, often used in the Netherlands, Belgium and Germany, consists of the individual concentrations of benzo(a)pyrene, fluoranthene, benzo(b)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene (RIVM, 1989).

2.5 Standards

It is clearly important to know what level of contamination is acceptable in order to make sure that any treatment process achieves a suitable standard. It would be easy to say that no contamination is acceptable but this requires a very precise and meaningful definition of what we mean by contaminated. No such definition is possible and it us usual, therefore, to assess the standards required according to its future placement. This may be anything from a landfill disposal site to beneficial placement on land, or from manufactured bricks to landscaping material. In most countries the standards required are assessed on a case by case basis but with some guidelines. Some of these are illustrated in the following table for sludges.

Table 2.2 Criteria for sludges applied to agricultural lands for selected countries

Parameter (kg/Ha)	UK	Netherlands	Germany	France	United States	Canada
Antimony						
Arsenic	10	2	-	-	-	15
Beryllium						
Cadmium	5	2.0	8.4	5.4	5-20	4
Chromium	1000	100	210	360	-	-
Copper	280	120	210	210	125-500	-
Iron						
Lead	1000	100	-	210	500-2000	100
Mercury	2.0	2.0	5.7	2.7	50-200	1.0
Nickel	70	20	60	60	-	36
Selenium	5	-	-	-	-	2.8
Silver						
Thallium						
Zinc	560	400	750	750	250-1000	370

2.5.1 Germany

The possibilities of beneficial use and disposal of dredged material depend in the fist instance on its physical and chemical properties. So far, Germany does not have a nation-wide regulation that summarises the criteria applied to different forms of dredged material management. Some of the beneficial uses are governed by special guidelines and criteria which are listed in the directive for the handling of dredged material on federal inland waterways in Germany (Koethe and Bertsch, 1997). The regulations mentioned below do not distinguish between direct beneficial use without pretreatment or treatment and beneficial use with pretreatment or treatment. Koethe and Bertsch review the regulations:

Use in agriculture and forestry:

- Technical rules of the LAENDER Working Group on Soil (LABO, 1996);
- The soil contamination thresholds of the Sewage Sludge Ordinance (AbfKlaer V, 1992);
- The stipulations of the Fertiliser Act (Dungemittelsgesetz, 1977) and the Ordinance on Fertilzer Application (Dungeverordnung, 1996) with a view to non-excessive nutrient supply;
- The criteria in the draft of the bylaws to the draft of the Federal Soil Protection Act (BMU,1997).

Use as a construction material

- Technical rules of the LAENDER Working Group for Wastes (LAGA, 1994). A ranking from Z0 to Z2 specifies utilisation classes. The LAGA criteria are given in the following table.

Table 2.3 German landfill classification for excavated soil material and underlying classification parameters (Z0-Z5) from LAGA (1994)

Error! Bookmark not defined. Class (upper limits)		Z0			Z1	Z2	Z3	Z4
			Z1.1	Z1.2				
			Restricted open placement			Landfill disposal		
		No restriction		In areas with favourable hydro-geological conditions with erosion controls	Restricted placement under defined technological precautions	Landfill class I (according to technical instructions for municipal waste)	Landfill class II (according to technical instructions for municipal waste)	Hazardous waste disposal facility (according to technical instruction for waste)
		Classification value for solids in excavated soil material						
Parameter								
Stability								
Shear strength	kN/m²	—	—	—	—	≥25	≥25	—
Axial deformation	%	—	—	—	—	≥20	≥20	—
Uniaxial compression strength/ resistance to compression	kN/m²	—	—	—	—	≥50	≥50	—
Organic content in the dry residue of the organic substance:								
measured by ignition loss	% Mass	—	—	—	—	≤3	≤5	—
measured as TOC	% Mass	—	—	—	—	≤1	≤3	—
Extractable lipophile substances in the original substance	% Mass	—	—	—	—	≤0.4	≤0.8	—
pH	mg/kg	5.5-8	5.5-8	5-9	—	—	—	—
EOX	mg/kg	1	3	10	15	—	—	—
Hydrocarbons	mg/kg	100	300	500	1000	—	—	—
Σ BTEX (benzene, toluene, ethanol, xyol)	mg/kg	<1	1	3	5	—	—	—
Σ Volatile chlorohydrocarbons	mg/kg	<1	1	3	5	—	—	—
Σ PAH	mg/kg	1	5	15	20	—	—	—
Σ PCB congener	mg/kg	0.02	0.1	0.5	1	—	—	—
Arsenic	mg/kg	20	30	50	150	—	—	—
Lead	mg/kg	100	200	300	1000	—	—	—
Cadmium	mg/kg	0.6	1	3	10	—	—	—
Chromium (total)	mg/kg	50	100	200	600	—	—	—
Copper	mg/kg	40	100	200	600	—	—	—
Nickel	mg/kg	40	100	200	600	—	—	—
Mercury	mg/kg	0.3	1	3	10	—	—	—
Thallium	mg/kg	0.5	1	3	10	—	—	—
Zinc	mg/kg	120	300	500	1500	—	—	—
Cyanides (total)	mg/kg	1	10	30	100	—	—	—
		Classification values for soil eluant						
PH		6.5-9	6.5-9	6-12	5.5-12	5.5-13	5.5-13	—
Electrical conductivity	µS/cm	500	500	1000	1500	≤10000	≤50000	—
Chloride	mg/l	10	10	20	30	—	—	—
Sulphate	mg/l	50	50	100	150	—	—	—
Cyanide (total)	µg/l	<10	10	50	100	—	—	—
Cyanides (free)	mg/l	—	—	—	—	≤0.1	≤0.5	—
Phenol index	µg/l	<10	10	50	100	—	—	—
Arsenic	µg/l	10	10	40	60	≤200	≤500	—
Lead	µg/l	20	40	100	200	≤300	≤1000	—
Cadmium	µg/l	2	2	5	10	≤50	≤100	—
Chromium (total)	µg/l	15	30	75	150	—	—	—
Chromium-VI	µg/l	—	—	—	—	≤50	≤100	—
Copper	µg/l	50	50	150	300	≤1000	≤5000	—
Nickel	µg/l	40	50	150	200	≤200	≤1000	—
Mercury	µg/l	0.2	0.2	1	2	≤5	≤20	—
Thallium	µg/l	<1	1	3	5	—	—	—
Zinc	µg/l	100	100	300	600	≤2000	≤5000	—
TOC	mg/l	—	—	—	—	≤20	≤100	—
Fluoride	mg/l	—	—	—	—	≤5	≤25	—
Ammonium N	mg/l	—	—	—	—	≤4	≤200	—
AOX	mg/l	—	—	—	—	≤0.3	≤1.5	—
Water soluble portion (Dry matter)	% Mass	—	—	—	—	≤3	≤6	—

Backfill in mines
The technical rules of the LAENDER Committee on Mining (Landerausschuss Bergbau, 1995) have to be considered.

Upland dumping
The criteria are fixed in the Technical Instructions on Municipal Waste (1993) and on Waste (1994) in form of rankings Z3 to Z5.

2.5.2 Netherlands

The following table (Table 2.4) is derived from the Dutch National Policy on Water Management (MTPW, 1989, cited in Donze et al 1990).

Lists have been prepared of concentrations corresponding to three provisional norms for sediment. These are:

- Quality objective 2000. This is a minimum standard, which, it is believed, can be achieved by the year 2000;
- Warning value. If this value for a parameter has been found additional research in the area will be necessary. Its use is to give direction to the monitoring programme;
- Test value. This is specifically used to judge the environmental acceptability of the sea disposal of dredged material.

A differentiation is made between substances on the M list and on the I list. The M list contains the most relevant problem substances for water management for which regular testing is necessary. The I list substances are of lesser concern and only require occasional testing.

Table 2.4 Quality objective 2000, test values and warning values for aquatic sediments in the Netherlands (After MTPW, 1989)

Parameters	**Concentration in sediment in ppm**			
	Quality objective 2000		**Provisional test value**	**Provisional warning value**
	M List	**I List**		
METALS				
Arsenic		85	85	150
Cadmium	2		7.5	30
Chromium	480		480	1000
Copper	35		90	400
Lead	530		530	1000
Mercury	0.5		1.6	15
Nickel	35		45	200
Zinc	480		1000	2500
PAH's				
Benzo(a)anthracene		0.05	0.8	3
Benzo(ghi)perylene	0.05		0.8	3
Benzo(a)pyrene	0.05		0/8	3
Phenathrene		0.05	0.8	3
Indeno(123cd)pyrene	0.05		0.8	3
Pyrene		0.05	0.8	3
Dibenzo(ah)anthracene		0.05	0.8	3
Anthracene		0.05	0.8	3
Benzo(b)fluoranthene	0.2		0.8	3

Benzo(k)fluoranthene	0.2		0.8	3
Chrysene		0.05	0.8	3
Fluoranthene	0.3		2.0	7
Sum PAH's (Borneff)	0.6		4.5	17
PCB's				
PCB 28	0.004		0.03	0.1
PCB 52	0.004		0.03	0.1
PCB 101	0.004		0.03	0.1
PCB 118	0.004		0.03	0.1
PCB 138	0.004		0.03	0.1
PCB 153	0.004		0.03	0.1
PCB 180	0.004		0.03	0.1
Sum PCBs (7)			0.2	0.4
PESTICIDES				
Aldrin + Dieldrin		0.04	0.04	0.5
Endrin		0.04	0.04	0.5
DDT + derivatives		0.01	0.02	0.5
a-endosulphane + sulphate	0.01		0.02	0.5
a-HCH			0.02	0.5
b-HCH			0.02	0.5
c-HCH	0.001		0.02	0.5
Heptachlor + epoxide		0.02	0.02	0.5
Chlorodana		0.02		
Hexachlorobutadiene		0.02	0.02	0.5
Total pesticides			0.1	2.5
DITHIOCARBAMATES				
Petroleum hydrocarbons	1000		3000	5000

The values stated in the table pertain to the content of sediment in the water bed converted to a standard sediment that contains 10% organic matter and 25% lutum (clay). A normalisation method is described in Section 2.5.4

2.5.3 United Kingdom

In the UK there are no legally binding standards for classifying dredged material in terms of levels of contamination. Guidelines on the disposal of dredged material to land have been published by the Construction Industry Research and Information Association (CIRIA, 1996). There are also several classification systems in current use (e.g. Kelly/Greater London Council, Greater Manchester Waste Regulation Authority (WRA), British Waterways (BW)). These systems are used for guidance rather than definition and are presented in Tables 2.2 to 2.5. Of these, only the British Waterways' system is directed at the disposal of dredged material.

a) Kelly (Table 2.5) and adaptations of it, such as the Greater Manchester WRA (Table 2.6), are mostly used to provide guidance on how contaminated the material is.

b) The Department of Environment's Interdepartmental Committee on the Redevelopment of Contaminated Land Classification (ICRCL) system (Table 2.7) was developed to be a decision-making tool for the redevelopment of derelict and/or contaminated land. However, the system's values of contaminants can be used for guidance on the disposal of dredged material and are mostly used for defining if dredged material is suitable for any of the end uses identified by ICRCL (i.e. for allotments/domestic gardens or paved areas for light industry).

c) BW has established a system specific to dredged material. It undertook a scheme to produce a national overview of dredging quality canals and navigations. The classification system was devised by integrating chemical quality criteria from the Kelly classification system, the ICRCL system and the agricultural use limits set by ADAS. The BW classification scheme (Table 2.8) provides guidance on the suitability of dredged material for specific uses.

British Waterways classification system

There are four classes under the British Waterways classification system (0, A, B and C).

Class 0	Material not characterised for various reasons, such as insufficient sediment or inaccessible at time of sampling.
Class A	Dredged material likely to be suitable for disposal to agricultural or land adjacent to canals.
Class B	Dredged material where concentration of contaminants is sufficiently low that the material can be used beneficially. Consequently such material is exempt from being a waste.
Class C	Dredged material classified as a waste and subject to controlled disposal.

The most stringent limits used are based on the DoEs Code of Practice for **Agricultural Sewage Sludge**. This code establishes the maximum concentrations of selected metals and metalloids which are permitted on soils used for agriculture. These standards originated for sewage sludge. They are presented in Table 1 and compared with those of other countries which also apply standards for disposal of sludges to agricultural land.

The BW system is derived for guidance and inclusion in one class does not prevent disposal by alternative options. For example, site characteristics may allow placement of material as if it were in a lower class. In addition, a system where leachability tests are to be undertaken and values established for contaminated materials may allow further flexibility within the disposal option.

It is important to understand the basis on which any characterisation or classification system is established. The BW classification system is derived using a range of values from the Kelly classification and the ICRCL mentioned previously. Explaining how these standards were derived is complex. However, the basic philosophy is to protect the receiving environment and human health. Kelly values are based on contaminant effects in respect of health risks and environmental hazards including direct ingestion, indirect ingestion, phytotoxicity, skin problems and effects on fauna. They were derived originally for guidance in interpreting various soil contaminants and the hazards they may pose for the development of contaminated land. These guidelines are widely known and applied throughout waste regulation bodies in the UK and in some cases, such as Greater Manchester WRA, have been extended to encompass other contaminants and applied to soils and other wastes.

Table 2.5 U.K. guidelines for contaminated soils - suggested range of values (Kelly classification system)

		Level of contamination			
Parameter	Typical values for uncontaminated soils	Slight	Contaminated	Heavy	Unusually heavy
pH (acid)	6-7	5-6	4-5	2-4	>2
pH (alk)	7-8	8-9	9-10	10-12	>12
Antimony	0-30	30-50	50-100	100-500	>500
Arsenic	0-30	30-50	50-100	100-500	>500
Cadmium	0-1	1-3	3-10	10-50	>50
Chromium	0-100	100-200	200-500	500-2500	>2500
Copper (avail)	0-100	100-200	200-500	500-2500	>2500
Lead	0-500	500-1000	1000-2000	2000-1.0%	>1.0%
Lead (avail)	0-200	200-500	500-1000	1000-5000	>5000
Mercury	0-1	1-3	3-10	10-50	>50
Nickel (avail)	0-20	20-50	50-200	200-1000	>1000
Zinc (avail)	0-250	250-500	500-1000	1000-5000	>5000
Zinc (equiv)	0-250	250-500	500-2000	2000-1.0%	>1.0%
Boron (avail)	0-2	2-5	5-50	50-250	>250
Selenium	0-1	1-3	3-10	10-50	>50
Barium	0-500	500-1000	1000-2000	2000-1.0%	>1.0%
Beryllium	0-5	5-10	10-20	20-50	>50
Manganese	0-500	500-1000	100-2000	2000-1.0%	>1.0%
Vanadium	0-100	100-200	200-500	500-2500	>2500
Magnesium	0-500	500-1000	1000-2000	2000-1.0%	>1.0%
Sulphate	0-2000	2000-5000	5000-1.0%	1.0-5.0%	>5.0%
Sulphur (free)	0-100	100-500	500-1000	1000-5000	>5000
Sulphide	0-10	10-20	20-100	100-500	>500
Cyanide (free)	0-1	1-5	5-50	50-100	>100
Cyanide (total)	0-5	5-25	25-250	250-500	>500
Ferricyanide	0-100	100-500	500-1000	1000-5000	>5000
Thiocyanate	0-10	10-50	50-100	100-500	>500
Coal Tar	0-500	500-1000	1000-2000	2000-1.0%	>1.0%
Phenol	0-1	2-5	5-50	50-250	>250
Toluene extract	0-5000	5000-1.0%	1.0-5.0%	5.0-25.0%	>25.0%
Cyclohexane extract	0-2000	2000-5000	5000-2.0%	2.0-10.0%	>10.0%

All concentrations mg/kg on air dried solids, except for pH.

Table 2.6 Greater Manchester WRA (UK): limits of ranges for contamination levels for soils and other wastes

	Class A	Class A	Class B	Class C	Class D	Class E
Determinant	Leach	Waste material	Waste material	Waste material	Waste material	Maximum
pH (acid)	5.5	6	5	4	2	2
pH (alkali)	9.5	8	9	10	12	14
Antimony	100	30	50	100	500	2,500
Arsenic	500	30	50	100	500	2,500
Barium	10,000	500	1,000	2,000	10,000	50,000
Beryllium	-	5	10	20	50	250
Boron (avail)	20,000	2	5	50	250	1,250
Cadmium	50	1	3	10	50	100
Chromium	500	100	200	500	2,500	12,500
Copper (avail)	30,000	100	200	500	2,500	12,500
Lead (avail)	500	200	500	1,000	5,000	25,000
Lead (total)	500	500	1,000	2,000	10,000	50,000
Magnesium	-	500	1,000	2,000	10,000	50,000
Manganese	500	500	1,000	2,000	10,000	50,000
Mercury	10	1	3	10	50	100
Nickel (avail)	500	20	50	200	1,000	5,000
Selenium	100	1	3	10	50	250
Vanadium	-	100	200	500	2,500	12,500
Zinc (avail)	50,000	250	500	1,000	5,000	25,000
Zinc (equiv)	50,000	250	500	2,000	10,000	50,000
Sulphate	2,500,000	2,000	5,000	10,000	50,000	250,000
Sulphur (free)	-	100	500	1,000	5,000	25,000
Sulphide	-	10	20	100	500	2,500
Cyanide (free)	500	1	5	50	100	500
Cyanide (total)	500	5	25	250	500	2,500
Ferricyanide	500	100	500	1,000	5,000	25,000
Thiocyanate	500	10	50	100	500	2,500
Coal Tar	-	500	1,000	2,000	10,000	50,000
Phenol	5	1	5	50	250	1,250
Toluene extract	100	5,000	10,000	50,000	250,000	500,000
Cyclohexane extract	100	2,000	5,000	20,000	100,000	500,000
PCBs	1	1	3	10	50	250
PAH's	2	50	500	1,000	5,000	25,000
Chlorinated solvents	30	1	3	10	50	250

All concentrations are maximum values.
All concentrations are in total values, unless otherwise stated.
All leach values, except pH, are in mg/l.
All waste material values, except pH, are in mg/kg (dry weight).

Table 2.7 ICRCL tentative trigger concentrations for selected contaminants

Contaminants		Planned uses	Trigger concentrations (mg/kg air-dried soil)	
			Threshold	Action
Group A: Contaminants which may pose hazards to health				
Arsenic		Domestic gardens, allotments	10	★
		Parks, playing fields, open space	40	★
Cadmium		Domestic gardens, allotments	3	★
		Parks, playing fields, open space	15	★
Chromium (**hexavelent**)		Domestic gardens, allotments	25	★
		Parks, playing fields, open space		
Chromium (total)		Domestic gardens, allotments	600	★
		Parks, playing fields, open space	1,000	★
Lead		Domestic gardens, allotments	500	★
		Parks, playing fields, open space	2,000	★
Mercury		Domestic gardens, allotments	1	★
		Parks, playing fields, open space	20	★
Selenium		Domestic gardens, allotments	3	★
		Parks, playing fields, open space	6	★
Group B: Contaminants which are phytotoxic but not normally hazardous to health				
Boron (water-soluble)	(3)	Any uses where plants are grown (2, 6)	3	★
Copper	(4, 5)	Any uses where plants are grown (2, 6)	130	★
Nickel	(4, 5)	Any uses where plants are grown (2, 6)	70	★
Zinc	(4, 5)	Any uses where plants are grown (2, 6)	300	★
Others				
Polyaromatic hydrocarbons	(7)	Domestic gardens, allotments, play areas.	50	500
		Landscaped areas, buildings, hard cover.		
			100	10,000
		Domestic gardens, allotments.		
Phenols		Landscaped areas, buildings, hard cover.		
			5	200
		Domestic gardens, allotments, landscaped areas.	5	1,000
		Buildings, hard cover.		
Free cyanide			25	500
		Domestic gardens, allotments.		
		Landscaped areas.	100	500
		Buildings, hard cover.		
Complex cyanides			250	1,000
		All proposed uses.	250	5,000
			250	NL
		Domestic gardens, allotments, landscaped areas.		
Thiocyanate			50	NL
		Buildings.		
Sulphate			2,000	10,000
		Hard cover.		
			2,000	50,000
		All proposed uses.		
			2,000	NL
		All proposed uses.		

Sulphide	Domestic gardens, allotments, landscaped areas. Buildings, hard cover.	250	1,000
Sulphur		5,000	20,000
Acidity (pH less than)		pH5	pH3
		NL	NL

Table 4: Notes

★ Action concentrations will be specified in the next edition of ICRCL 59/83.
1. Soluble **hexavalent** chromium extracted by 0.1M HCl at 37°C: solution adjusted to pH 1.0 if alkaline substances present.
2. The soil pH value is assumed to be about 6.5 and should be maintained at this value. If the pH falls, the toxic effects and the uptake of these elements will be increased.
3. Determined by standard ADAS method (soluble in hot water).
4. Total concentration (extractable by $NHO_3/HClO_4$).
5. The phytotoxic effects of copper, nickel and zinc may be additive. The trigger values given here are those applicable to the 'worst case': phytotoxic effects may occur at these concentrations in acid, sandy soils. In neutral or alkaline soils phytotoxic effects are unlikely at these concentrations.
6. Grass is more resistant to phytotoxic effects than are most other plants and its growth may not be adversely affected at these concentrations.
7. Used here as a marker for coal tar, for analytical reasons.

NL No limit set as the contaminant does not pose a particular hazard for this use.

Table 2.8 The British Waterways classification system for sediment

Class	Criteria
0	Not sampled either owing to: lack of sediment, or area inaccessible at time of survey (e.g. sample in tunnel).
A	Complies with agricultural use limits at pH <5* and does not exceed ICRCL thresholds. In addition, does not have a Kelly rating greater than 0.3.
B	Complies with ICRCL thresholds with the exception of zinc, nickel, copper and boron. Threshold values for these phytotoxins are derived from ICRCL 70/90. Does not necessarily comply with thresholds for phenol and sulphide as ICRCL recommended methodology is inappropriate for organic-rich wet sediments. No single parameter in range of 'unusually heavily contaminated' as defined by Kelly (1979). Does not have an overall Kelly rating greater than 1.5.
C	Exceeds ICRCL threshold for parameters other than zinc, nickel, copper, phenol and sulphide. Has a Kelly rating greater than 1.5 and/or has one parameter in range of 'unusually heavily contaminated' as defined by Kelly (1979).
Class	**Disposal Characteristics**
A	Sediment likely to be suitable for disposal to agricultural land or adjacent land.
B	Sediment where concentrations of contamination are such that the sediment is likely to be suitable for disposal under exemption from the Waste Management Licensing Regulations, 1994.
C	Sediment where concentrations of contamination are such that the sediment is unlikely to be suitable for disposal under exemption from the Waste Management Licensing Regulations, 1994. Further investigation may be required.

* Lower pH values lead to greater mobility of metals.

2.5.4 Normalisation

Conversion allows application of the various standards to sediments of different physical composition. The reason for conversion lies in the fact that the contaminants usually adhere to the finer fractions in the sediment. It is quite normal for sediment containing a high percentage of fine material and a high organic content to show higher concentrations of contaminants compared to say a sandy material. The reasons for this are described in Section 2.2.1. Some standards specify the dividing particle size for analysis, eg < 0.002 mm is recommended by PIANC (1996). Where no common basis exists data may be compared and assessed relative to standards by normalising. The normalising process used by the Dutch is given in Donze et al (1990).

For heavy metals

$$Cc = C.\ \frac{(a + b.l + c.org)}{(a + 25b + 10c)}$$

Where:

C	Measured metal concentration (ppm)
Cc	Corrected value of S
a,b,c	Constants depending on the element. The values are given in Table 2.9 Below
l	lutum (clay) content (%)
org	organic content (%)

Table 2.9 Constants for normalisation of heavy metal content after MTPW (1989)

Metal	**Constants**		
	a	**b**	**C**
As	15	0.4	0.4
Cd	0.4	0.007	0.021
Cr	50	2	0
Cu	15	0.6	0.6
Hg	0.2	0.0034	0.0017
Ni	10	1	0
Pb	50	1	1
Zn	50	3	1.5

The above table illustrates that Chromium and Nickel are not correlated with organic matter and that Arsenic, Copper and Lead are equally correlated with lutum and organic matter.

Organic micropollutants

Organic micropollutants are correlated with organic content and not with clay. The normalisation is therefore a simple matter of scaling the measured content to the standard organic content (10%), for example if the actual sample contained 5% organics the measured concentration of micropollutants should be doubled to give the equivalent concentration in a sample containing 10% organics.

3. TECHNOLOGIES

The technologies for treating contaminated sediment are considered in two phases. The first phase is pre-treatment. There are two primary reasons for pre-treating contaminated sediments. The first is to condition the material so that it meets the requirements of the treatment process. Most technologies require that the feed material be relatively homogeneous and that its physical characteristics (eg solids content, particle size) are within a narrow range for efficient processing. The second reason is to reduce the volume of sediments that require transport, treatment or special disposal. In the latter case this may be considered as treatment rather than pre-treatment since no further treatment is envisaged. However, the distinction is not important in considering the technologies.

There are numerous treatment technologies. Many have been developed for cleaning up contaminated soils or waste sites. The differences have already been discussed briefly in Section 1.7. The list of technologies is continually changing as new ones become available and others withdrawn.

A number of useful databases exist (USEPA , 1994):

Sediment Treatment Technologies Database (SEDTEC)
Available from:
Wastewater Technology Centre
867 Lakeshore Road
Burlington, Ontario L7R 4L7

Sponsored by:
Environment Canada, Great Lakes Clean-up Fund

Description:
Currently in its second edition, SEDTEC provides fact sheets on 168 different technologies submitted to the Wastewater Technology Centre from vendors and technology developers around the world.

Vendor Information System for Innovative Treatment Technologies (VISIT)
Available from:
PRC Environment Management Inc
1505 PRC Drive
McLean, Virginia 22102

Sponsored by:
US Environment Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, DC 20460

Description:
Similar to SEDTEC, except that only innovative technologies are included and technologies are not specific to sediments. The current version 1.0 contains 94 technologies for treating sediments. Specific performance data may be included.

Risk Reduction Engineering Laboratory (RREL) Treatability Database
Available from:
US Environment Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

Description:
Provides results of published treatability studies that have passed the USEPA's quality assurance review. Although the most current data are for wastewater treatment, recently available treatment for soils and sediments will be added in future updates.

Pretreatment technologies are described in Section 3.1 and treatment technologies in Section 3.2.

3.1 Pretreatment technologies

Pretreatment technologies may be used to modify the physical characteristics of the feed material to meet the needs of the treatment process. This may also be called "conditioning" the sediment. Examples of the requirements are shown in Table 3.1

Table 3.1 Example feed material

Technology	Maximum particle size cm	Optimal solids content %
Chemical extraction[a]	0.6	>20
Thermal desorption	0.6	50-100
Incineration	15	95-100
Chemical treatment (K-Peg)[b]	2.5	>80
Immobilisation	15	>60
Hydrocyclone	Note c	5-25

a Based on Basic Extractive Sludge Treatment (BEST) process (USACE, 1994, Diez, 1994).
b Based on alkaline metal hydroxide/polythene glycol (APEG) process (USEPA 1991).
c Not more than one quarter of the diameter of the hydrocyclone apex (discharge) opening, or smaller if required for protection of the pump.

There are two main types of pretreatment, dewatering and physical separation aimed at meeting the above criteria.

3.1.1 Dewatering technologies

Mechanically dredged sediments typically have a solids content comparable to that of in situ sediments (about 50% by weight for most fine grained sediments). Hydraulically dredged sediments are in a slurry with a solids content typically in the range 10-20%. Some hydraulic dredge pumps are able to move slurries with higher solids content. They are often termed "environmental dredgers" and are particularly useful for small quantities of contaminated sediment in shallow water (eg marinas). Dewatering also reduces the volume of the material which decreases the costs of transport. The water removed may be contaminated and itself require treatment.

The process of dewatering is often a driving force for other changes. As drying takes place cracks develop which allow air penetration which changes anaerobic conditions to aerobic conditions. Oxidation takes place and biological changes take place which generally reduce the level of some contaminants. Further discussion on this aspect is given in Section 3.2.9

3.1.1.1 Passive dewatering

This refers to those dewatering techniques that rely on natural evaporation and drainage to remove moisture. Drainage may be by gravity or may be assisted by pumping. Mechanical disturbance is also used, such as trenching and ploughing.

It has traditionally been accomplished in confined disposal facilities (CDF's) which rely on primary settling, surface drainage, consolidation and evaporation. Subsurface drainage and wicks (vertical drainage) are also used. These require quite large amounts of land because to be effective they require the material to be placed in thin layers or "lifts".

Sediments can also be dewatered in temporary holding tanks and lagoons.

Surface drainage:
In most cases natural drainage through permeable boundaries such as dykes will not be permitted. Surface water is normally drained to discharge points which may include overflow weirs, filter cells or pump control structures. Drainage water will include not only the water from the sediment but rainfall. Progressive trenching speeds drainage and aids evaporation.

Evaporative drying:
The desiccation of dredged material by evaporative drying results in the formation of a crust at the sediment surface. This method of drying is a two stage process. The first stage occurs until all free standing water has been decanted from the dredged material surface. Pore water has been squeezed out by the settling and consolidation process at a higher rate than drainage and evaporation. The corresponding void ratio at this point is termed the initial void ratio (e_{00}) and has been determined to occur at a water content of approximately 2.5 times the Atterberg liquid limit of the material. The second stage of drying occurs until the material reaches a void ratio called the desiccation limit (e_{dl}). At this point evaporation of any additional water from the dredged material will effectively cease. The e_{dl} corresponds to a water content of 1.2 times the Atterburg plastic limit (USACE 1987). The thickness of the crust and drying rate depend on local conditions and sediment properties. The rates can be estimated using the Primary Consolidation and Desiccation of Dredged Fill (PCDDF) module of the Automated Dredging and Disposal Alternatives Management System (ADDAMS) model (Schroeder and Palermo, 1990).

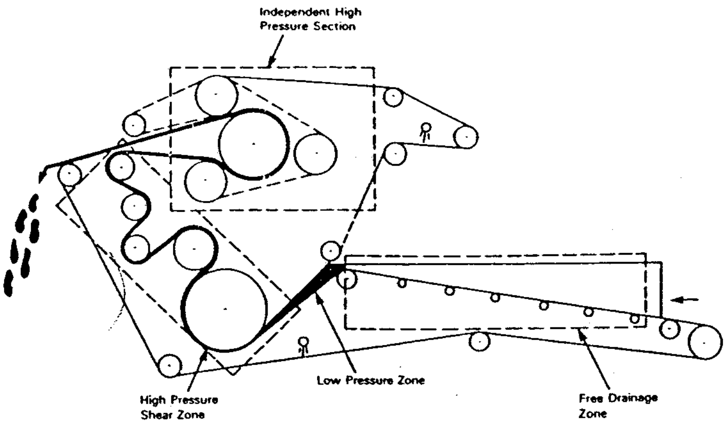
Subsurface drainage:
One approach is to place perforated pipes under or around the perimeter of a CDF that drain into a series of sumps from which water is withdrawn. The pipes can be placed in a layer or trenches of drainage material, typically sand or gravel. The feasibility may be limited where several layers of fine dredged material are placed because the drains may become clogged.

There are several variations on subsurface drainage systems, including the gravity underdrain, vacuum assisted underdrain, vacuum assisted drying beds and electro-osmosis. The gravity underdrain system provides free drainage at the base of the dredged material. The vacuum assisted version is the same but uses an induced partial vacuum in the layer which can improve dewatering efficiency by 50%, but requires considerable maintenance and supervision (Haliburton, 1978).

Wick drains:
Wick drains or "wicks" are polymeric vertical strips that provide a conduit for upward transport of pore water which is under pressure from the overlying weight of material. By placing vertical strips at about 1.5m centres to depths of 12m, both vertical and radial drainage are promoted. Wick drains can reduce consolidation time by a factor of 10 (Koerner et al, 1986).

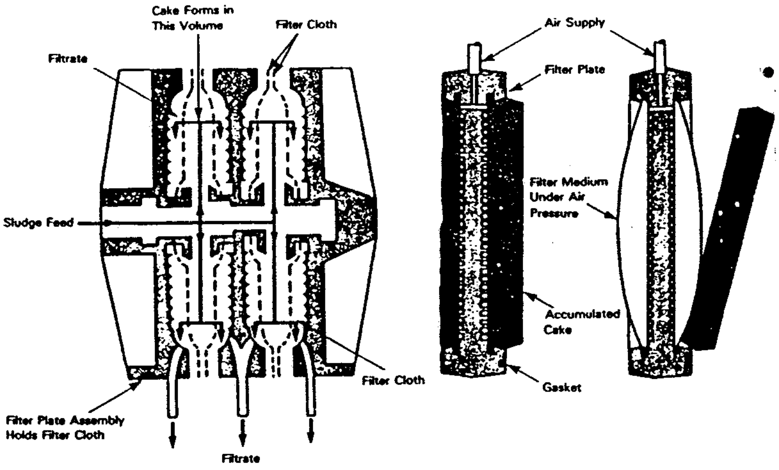
3.1.1.2 Mechanical dewatering technologies

These are used extensively for conditioning municipal and industrial sludges and slurries as well as in mineral processing applications. They require input of energy to squeeze, press or draw water from the feed material. Generally they are able to increase the solids content to a maximum of about 70% by weight. Six mechanical dewatering processes are illustrated in Fig 3.1(a-f).



- Uses single- or double-moving belts to dewater sludges. With double-moving belt, upper belt operates as the press belt and lower belt operates as the filter belt
- A flocculant is injected to condition the solids in a mix tank positioned in front of the belt filter
- Dewatering occurs in three stages: 1) gravity drainage of free water, 2) low-pressure compression, and 3) high-pressure compression and shear; the dewatered solids are discharged from the high-pressure zone
- Important operational variables include: belt speed, feed concentration, polymer conditioner type and dosage, belt characteristics (type, tension), and washwater flow

Belt Filter Press

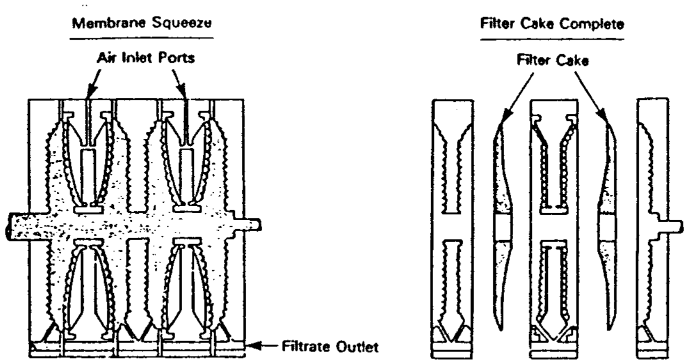


- Uses rigid individual filtration chambers operated in parallel under high pressure
- Consists of parallel vertical plates placed in series and covered on both sides with replaceable fabric filters; slurry is pumped under pressure into the press and passes through feed pores in trays that lie along the length; water flows through the filter media while solids form a cake on the filter's surface; when dewatering ceases, the filter press is opened and individual vertical plates are moved sequentially over a gap allowing the caked solids to fall off; after the cake is removed, the plates are pushed back into place and the press is closed for the next dewatering cycle
- Important operational variables include: feed pressure, filtration time, conditioner type and dosage, use of precoat, and type of filter cloth

Recessed Plate Filter

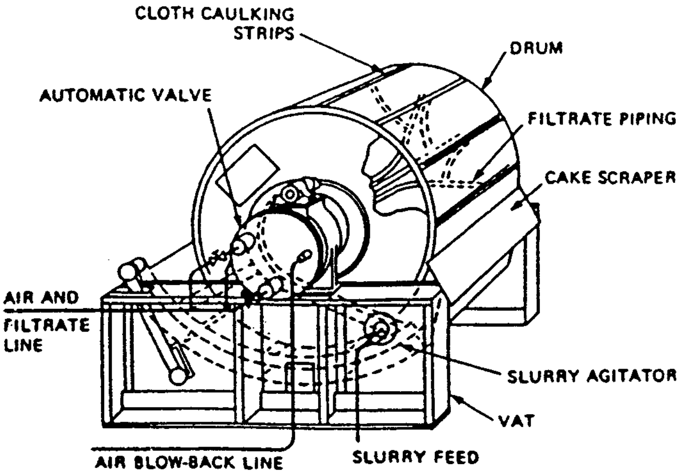
Figure 3.1 Mechanical dewatering technologies

Diaphragm Plate Filter



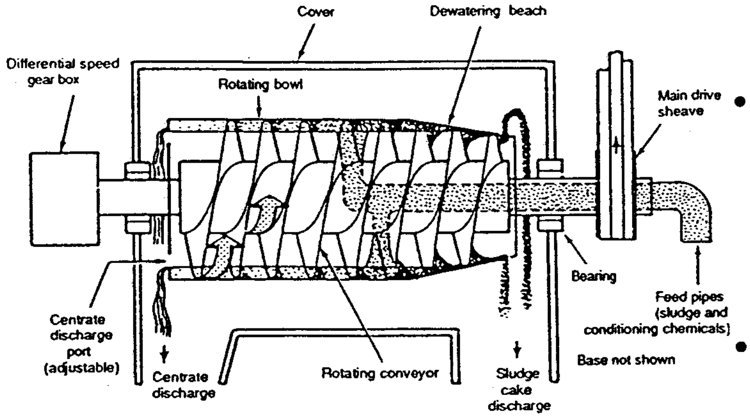
- Commercialized in the United States in the 1980s
- Similar to the recessed plate filter, except that an inflatable diaphragm is incorporated into the design; at the end of the pumping cycle, pressures up to 14–17 atmospheres (1.4–1.7 MPa) are applied to the diaphragm for additional dewatering
- Percent solids usually 5-8 percent higher compared to conventional filter press; also, organic polymers, rather than ferric salts and lime, may be used as conditioners
- Important operational variables include: diaphragm and feed sludge pressures, conditioner type and dosage, filtration and diaphragm squeezing times, and type of filter cloth

Vacuum Filter



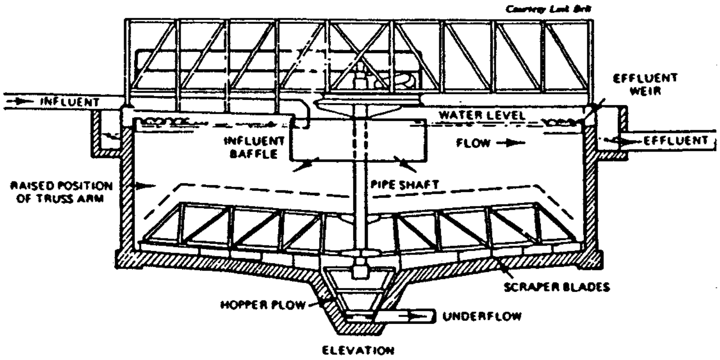
- Continuous process with self-cleaning filter media consists of a rotating cylindrical drum mounted horizontally and partially submerged in a trough containing a slurry; the drum, covered by fabric or wire mesh, allows moist solids to adhere via negative pressure from a vacuum supply; water flows through the filter into the center of the drum and exits the unit for further treatment or disposal; solids are scraped off the drum as it rotates
- Usually requires ferric salt and/or lime conditioner
- Important operational parameters include: drum submergence, drum speed/cycle time, solids content in feed, washwater quantity, conditioning chemicals, and filter media used

Figure 3.1 Mechanical dewatering technologies (continued)



- Uses rapid rotation of a fluid mixture inside a rigid vessel to separate the components based on their mass
- Centrifuges are generally used in conjunction with flocculants and can be used to dewater or concentrate soils and sediments ranging in decreasing size from fine gravel to silt; incorporation of a paper cloth filter in the centrifuge or the injection of flocculants improves the recovery and removal efficiencies
- The solid bowl centrifuge is most commonly used for dewatering, although other designs (basket and disc) are available
- Important operational variables for solid bowl centrifuges are: bowl/scroll differential speed, pool depth, polymer dosage, and point of addition

Centrifugation



- Operates on differences in specific gravity between solids and water to accomplish separation; an effluent with a reduced concentration of suspended solids is produced and removed while a thickened mass of solids remains in a smaller slurry volume
- Gravity thickening usually occurs in a circular vessel constructed of concrete or steel designed similarly to a conventional clarifier; slurry is pumped into a feed well and allowed to thicken via gravity settling; clarified liquid overflows an effluent weir and leaves through an effluent pipe, while the concentrated sludge is raked to the center of the vessel and discharged by gravity or pumping
- Important operational parameters include: polymer dosage and overflow rate

Gravity Thickening

Figure 3.1 Mechanical dewatering technologies (continued)

Several systems for mechanical dewatering were investigated for use with contaminated sediments from the Ghent –Terneuzen Canal, Belgium (Malherbe et al, 1988). They were:

- Chamber filter presses;
- Belt filter press;
- Centrifuge.

The highest volume reduction, up to 50%, was obtained with the chamber filter presses. Because of the contamination with metals special attention had to be paid to their behaviour during dewatering. Analyses carried out on the filtrate and the filtercake showed that the metals were mainly concentrated in the filtercake. The metals also seemed to concentrate more at high filtration pressures. This was especially true for copper, lead and zinc.

A chemical conditioner may be added to improve the efficiency of the process. With inorganic material the dosage of lime and ferric chloride may be as high as 20% (Dick, 1972). In the case of the Ghent-Terneuzen Canal laboratory tests were carried out to determine the optimum doses (Malherbe et al, 1988) but the results are not quoted in the literature.

A high solids capture is desirable because solids lost from the process (i.e. in the filtrate or centrate) represent a route for contaminants to enter the environment. Some particulate loss during mechanical dewatering is inevitable therefore the effluent must be treated.

Most processes work best at constant rate with a homogeneous material. Because hydraulic dredging produces highly variable flow rates and solids concentration, direct dewatering would be inappropriate. Temporary storage in a tank or lagoon or a CDF would be necessary to even out the flows and concentration prior to further dewatering by mechanical means.

Mechanical dewatering has been tested in the US on a limited scale. A vacuum filtration unit was tested on sediments from Toledo Harbour, Ohio (Long and Grana, 1978). The solids content prior to conditioning with lime ranged from 15-23%. The post treatment solids content was consistently above 43%. A 2.5m wide filter press was demonstrated on sediment from the Ashtabula River in Ohio at a rate of 23 tonnes/hr. Solids were increased to 50-60% with losses of around 2-5% (Rexnord, 1986).

A substantial amount of design and operation guidance on mechanical dewatering systems is available for municipal, industrial and mineral processing applications (Weiss, 1986) but there are some fundamental differences between sludges and sediments, including:

- Sediments are less compressible, less gelatinous and lower in organic content and are thus easier to dewater;
- The solids content will be higher for sediments (15-20% compared to 3-6% for sewage treatment);
- Sediments can contain rocks and large particles that can interfere with or damage equipment (see screening and debris removal Section 3.1.2);
- Municipal sludges are generated at a more or less steady rate whereas dredging is usually over a short period and may be a "one off" exercise;
- Disposal of wastewater and filtrate is a minor problem for municipal sludges, because it can be returned to the treatment process whereas wastewater from sediments is a major concern and may require separate treatment.

3.1.1.3 Active evaporative technologies

Active evaporation is different from passive evaporation used in CDF's in that artificial energy sources are used to heat the sediments, as opposed to solar radiation. Active evaporation is the most expensive dewatering technology but has been used to prepare municipal sludges for incineration or for sale of fertiliser (Dick, 1972). Nearly all the water is removed, resulting in a solids content of about 90%. The technologies which might be applicable to sediment are:

- Flash dryers;
- Rotary dryers;

- Modified multiple hearth furnaces;
- Heated auger dryers.

These have not been demonstrated with sediments on any scale. Most of the design and operating guidance are from municipal and industrial waste applications (USEPA, 1987).

3.1.1.4 Choosing the most appropriate dewatering technology

The main choice is between a passive and a mechanical method. Active evaporative technologies would only be employed where subsequent processes (eg thermal desorption or incineration) require extremely dry materials. The advantages and disadvantages of passive and mechanical dewatering are listed in Table 3.2 reproduced from EPA, 1994, while the advantages and disadvantages of mechanical dewatering technologies are given in Table 3.3.

Table 3.2 Advantages and disadvantages of passive and mechanical dewatering

Advantages	Disadvantages
Passive dewatering	
Able to dewater large quantities of sediments concurrently. Very low operating costs. Can accommodate high flow rates and rapidly varying flows and solids concentration such as those produced from a hydraulic dredger. The site used for can provide intermediate storage and, in the case of confined disposal facilities, a final disposal site for dredged material.	Land area requirements are large. Dewatering times range from moths to years Material must be excavated if subsequent treatment and/or disposal is to take place. Contaminant loss by volatilisation is not easily controlled.
Mechanical dewatering	
Provides a method of increasing sediment solids content quickly and efficiently. Requires small space. Contaminant losses, including volatile losses, can be controlled.	Fine-grained sediments may bind or clog filters. Equipment is usually housed in a building. Operator attention is required. Requires conditioning chemicals that may increase the weight of dry solids. Dewatered solids must be removed on a continuous or semi-continuous basis.

Table 3.3 Selection of mechanical dewatering technology

Technology	Cake solids %	Solids recovery %	Advantages and Disadvantages
Belt Filter Press	31-38[a] 30-90[b]	90-95[a]	Generally best suited for mobile treatment systems. Performance is sensitive to feed characteristics and chemical conditions. Belts can deteriorate quickly in the presence of abrasive material. Clogging with fines or oily material can occur. Generates a substantial amount of was water that must be treated.
Filter Press Recessed Plate	40-46[a] up to 90[b]	98+[a]	Available in portable units. Costly and energy intensive. Replacement of filter media is time consuming. Clogging with fines or oily materials can occur. Generates waste water that must be treated.
Filter Press Diaphragm	45-50a up to 90b	98+[a]	
Filter Press Batch plate and frame filter	up to 90b	NA	
Vacuum filtration	25-33[a] up to 70[b]	85-90[a]	Vacuum disc and drum filters account for about 90% of mineral processing filtration units. Filter media blinding can be eliminated by use of continuous drum filter. Vacuum filtration less effective than other dewatering technologies with sewage sludge.
Solid bowl centrifuge	29-36[a]	90-95[a]	Adaptable to either thickening or dewatering slurries. Suitable for areas with space limitations. Most compatible with oily solids. Process may result in a buildup of fines in effluent from centrifuge. Scroll is subject to erosion.
Gravity thickening	10-18[a] 15-50[b]	NA	Effective method for thickening sediment slurries. Traditional thickeners require much space but high rate and lamella thickeners occupy much less space. Potential for localised odour and air pollution problems.

3.1.1.5 Costs

Price range for passive dewatering is too site specific to give a good indication. EPA (1994) suggests about $128,000 for a 41hectare CDF with 70% operating efficiency and 20% administrative surcharge.

Mechanical dewatering costs are in the range \$8 - \$27 per m^3 of slurry, depending mainly on the solids content of the feed material (range say 10 – 40%).

3.1.2 Physical separation

Physical separation technologies are used to remove oversized material and debris in order to produce an acceptable feed material for further handling and treatment. These technologies are also used to separate the sediments into two or more fractions based on physical properties or characteristics to reduce the quantity of material requiring treatment or confined disposal. For example the MEHTA processing plant in Hamburg, Germany operates on the principle that the contaminants are contained primarily in the fine sediment so separation of this fraction allows disposal or beneficial use of the sand fraction while giving a reduced volume of contaminated mud to deal with.

The effectiveness of separation has been studied by Cuperus et al (1997). It is noted that contaminants can bind into a dredged material matrix in a number of ways. They may for instance be present in the form of an individual free phase (eg PAH) particles. Monitoring was carried out of the separation of three batches of dredged material. During the separation process samples were collected at various points in the installation, before and after the units. The samples were extensively analysed in the laboratory.

In these tests the separator was set at a diameter of 0.040 to 0.050mm. This stage is the most significant for separating the <0.063 mm material. The sand fraction separated at the bottom of the classifier does not contain any organic matter and almost no <0.063 mm particles. However, the speciation of the different mineral particle size fraction shows that the part of the mineral fraction is separated via the upper effluent streams of the separators and the classifier and via the sieve deck. This loss of sand is caused by a number of factors:

- Insufficient performance of the individual installation units
- The dragging along of coarser mineral parts during the separation of agglomerates in the sieve deck and during the separation of organic material in the separator and classifier.

The extent to which a separator is capable of separating organic matter partly depends on the way in which the organic matter is present. The organic matter found in the upper effluent stream of the separator mostly consists of small particles, whereas the coarser organic matter particles are mostly found in the bottom stream of the separator. Owing to the lower density of the organic particles compared to that of the mineral particles in the bottom stream of the separator, in the classifier fraction is completely separated from the mineral one.

Cuperus (1997) notes the following important points concerning the behaviour of contaminants during separation:

> **Speciation of dry matter compared to that of contaminants**
> Organic matter, heavy metals, PAH and mineral oil concentrate in the upper streams of the separator and classifier. Calcium carbonate is not or hardly concentrated there. It also appears that PAH and mineral oil are primarily separated by the classifier, along with organic matter. Heavy metals are separated to the same extent by the upper streams of both the separator and the classifier.
>
> **Binding of contaminants**
> Copper, mercury and nickel are primarily bound in or on organic matter and sulphides; lead is primarily bound to iron and/or manganese (hydr-)oxides; most of the zinc is bound to to/on organic matter, sulphides, iron and/or manganese (hydr-)oxides. Heavy metals actually do concentrate in the same fractions in which organic matter and iron and/or manganese (hydr-)oxides are concentrated. There is, however, no evidence of a clear relation between the degree of concentration of the heavy metals and that of organic matter/ iron and/or manganese (hydr-)oxides.

Binding of contaminants to organic matter

Mineral oil and PAH particularly concentrated in the fractions where organic matter was found. Based on this observation it can be concluded that it must be possible to remove PAH and mineral oil from contaminated dredged material by separating off the organic matter. Heavy metals also appear to bind to organic matter to a significant degree. They do, however, also occur in other types of bonds. If the exact binding forms in which heavy metals occur are known, it is basically possible to predict the extent to which heavy metals can be removed from the sand fraction in a separation installation.

Binding of contaminants to the mineral fraction

Heavy metals that are not bound to organic matter and/or sulphides are primarily bound to the iron and/or manganese (hydr-) oxides. The configuration of the plant did not allow separation from the organic matter so it was not possible to establish a relationship.

Some additional conclusions were:

- The installation tested was capable of recovering sand out of which all organic matter and almost all clay have been removed. Division according to particle size mainly occurs in the separators, whereas the classifier sorts according to density.

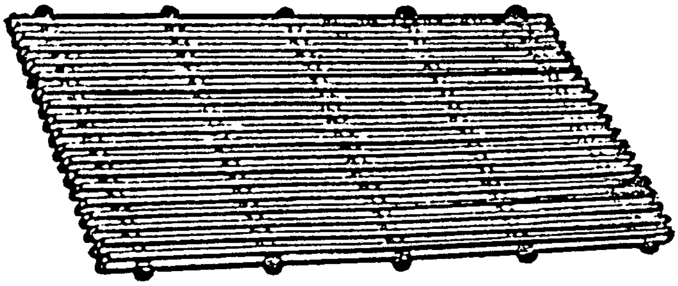
- Insufficient disaggregation can lead to losses in sand. This can be overcome by adding more energy.

- The sand recovered still contains a small amount of heavy metals. These metals (particularly lead and zinc) are mainly bound to iron (hydr-)oxides, carbonates and to some extent to the fraction <0.063mm. The efficiency with which this fraction is removed can be increased by fine tuning the installation.

- As mineral oil and PAH are almost completely bound to organic matter, they are almost completely removed from the sand fraction together with the organic matter. Most of the heavy metal content also appeared to be bound to the organic matter (albeit to a lesser extent than oil and PAH).

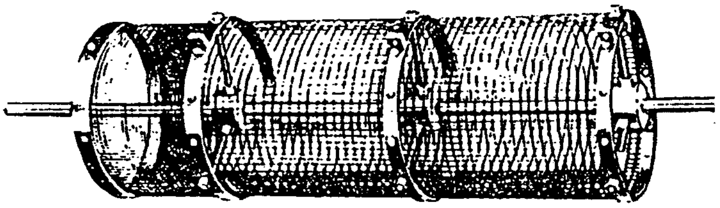
With these limitations in mind, six types of separation technology are now considered:
- Debris removal;
- Screens and classifiers;
- Hydrocyclones;
- Gravity separation;
- Froth flotation;
- Magnetic separation.

These are illustrated in Fig 3.2(a-f) and discussed in the following sections.



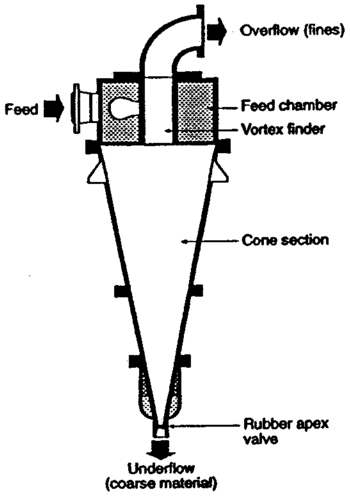
- Grizzlies are composed of parallel iron or steel bars, usually inclined, of 2- to 30-cm spacing
- Used for very coarse separations
- The most common application in mineral processing is to "scalp" the feed to a primary crusher, which prevents clogging and improves capacity by removing feed material smaller than the crusher's product size
- Can be used to screen cobbles, rock, and debris from sediments

Grizzly



- Rotating, slightly inclined cylinder of sturdy wire mesh, with openings from 6 to 55 mm across
- Trommels have poor capacities, because only part of the screen surface is used at any one time
- Rugged, inexpensive, and relatively free of maintenance

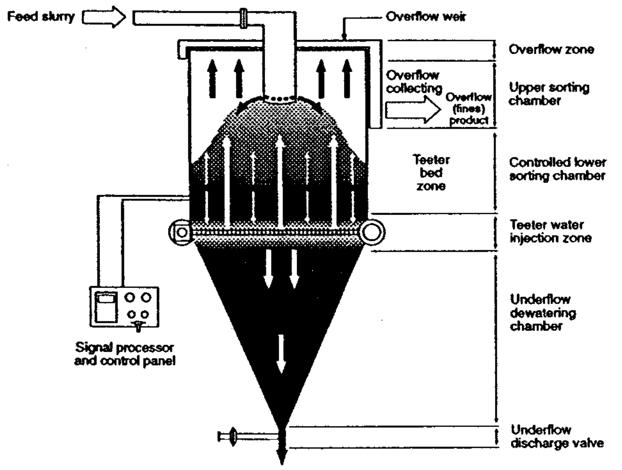
Trommel



- High-throughput, continuously operating size classification device that uses centrifugal force to accelerate the settling rate of particles
- Widely used in the mineral processing industry
- Most common applications make separations from 40–400 μm in particle diameter, although separations as fine as 5 μm, or as coarse as 1,000 μm, are well known
- Capacity (200–13,500 L/min) is dependent on diameter
- There are more than 50 hydrocyclone manufacturers worldwide (Edmiston 1983)

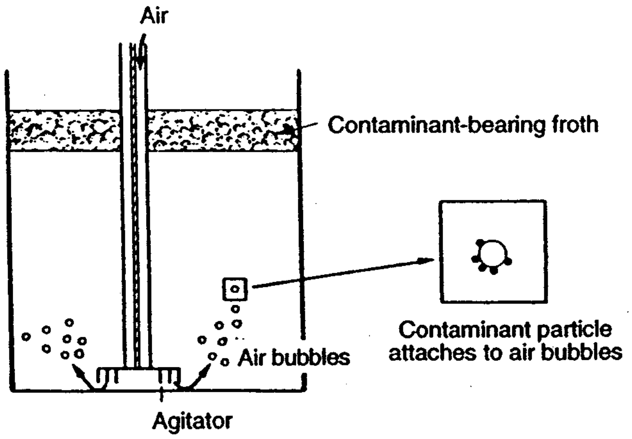
Hydrocyclone

Figure 3.2 Physical separation technologies



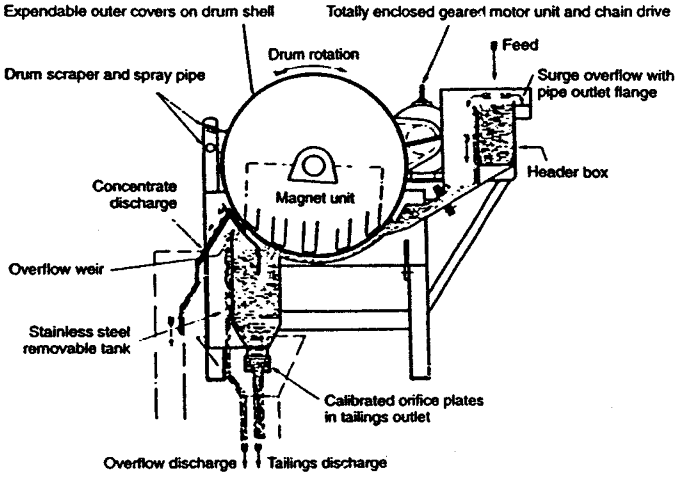
- Separates particles based on density differences
- Works best on particles larger than 75 μm, but separations among particles as small as 10 μm can be achieved at low capacity with certain equipment
- Equipment commonly used includes dense medium separators (as shown), jigs, shaking tables, flowing film concentrators, centrifugal separators, and elutriators

Gravity Separator



- Used to process millions of tonnes of ore daily
- Flotation successfully applied to particles as small as 10 μm
- Almost all flotation is conducted in stirred, aerated tanks of up to 56 m^3 (2,000 ft^3), although vertical columns and air-sparged hydrocyclones are used occasionally

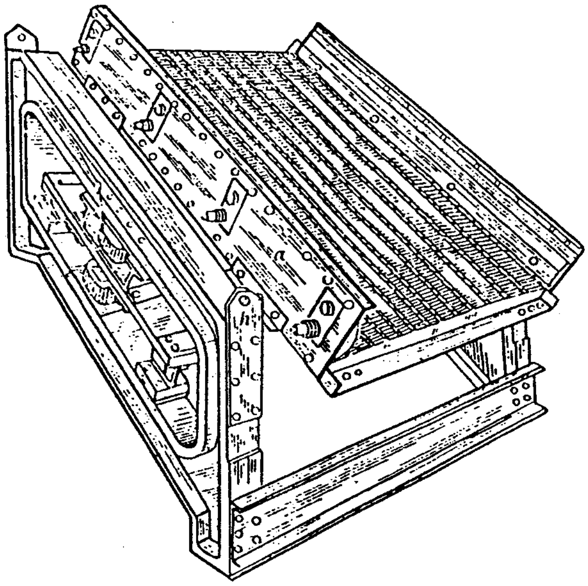
Froth Flotation



- Low-intensity separators (as shown) employ permanent magnets, and are most often used for material coarser than about 75 μm of high magnetic susceptibility, such as iron ore
- Rotating drum separators (as shown) commonly used for wet applications
- High-intensity separations employ electromagnets and are much more versatile and capable of recovering iron-stained or rusted silicate minerals from other purer, nonmagnetic phases

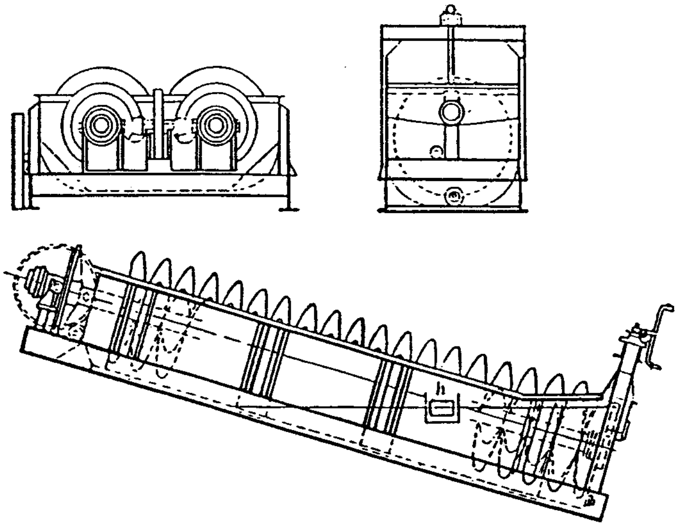
Drum-type Magnetic Separator

Figure 3.2 **Physical separation technologies (continued)**



Vibrating Screen

- Reciprocating, gyrating, and vibrating screens are used to make wet or dry separations from 25 cm down to 40 μm
- Can be stacked to produce multiple sized products
- May have very limited throughput, particularly when there is a large amount of material near the size of the mesh opening
- Blinding of screens is a frequent problem, and is controlled in some applications with a "ball tray" (a tray of hard rubber balls that continually bounce against the underside of the screen fabric to dislodge stuck particles)
- Screen cloth is subject to extreme wear and requires frequent replacement (Wills 1988)



Spiral Classifier

- Mechanical classifiers are based on the differing terminal settling velocities of dissimilar particles in a fluid, usually water
- A rake or screw (as shown) is used to drag the fastest settling (and therefore largest) particles up an incline against the fluid flow; slower-settling (and therefore smaller) particles travel with the fluid flow out of the device through an overflow weir
- Operate at less than 50-percent solids by weight (careful control of slurry density is of the utmost importance, especially in making very fine separations)
- Effective particle size range is approximately 50–1,500 μm

Figure 3.2 Physical separation technologies (continued)

3.1.2.1 Debris removal technologies

Examples of debris commonly encountered in dredged material include cobbles, bricks, large rocks, tyres, cables, bicycles, shopping trolleys, steel drums, timbers, scrap metal and even whole cars. Near docks and loading areas bulk materials may also be found such as coal or gravel and various other bulk products.

Debris must be removed and the size requirement for treatment processes is given in Table 3.1. Debris can be removed at various stages from on board to the dredger to post processing after initial placement. The technologies available include:
- Drag line;
- Grapple bucket;
- Mechanical removal;
- Screens (discussed below).

These are fairly simple and their function is self explanatory.

3.1.2.2 Screens and classifiers

While hydrocyclones are the most popular separation device, grizzlies, trommels, vibrating screens and mechanical classifiers are all widely used in mineral processing applications. Screens and classifiers may be the first units in a complex separation process or the only units in a simple process. A trommel and vibrating screen were used in the ARCS Program demonstration at Saginaw, Michigan (USACE Detroit, 1994). A grizzly, vibrating screen and screw classifier were used at a sediment remediation demonstration project at Welland, Ontario (Acres International, 1993).

Grizzlies

Grizzlies are the simplest and coarsest devices for removing small debris. They can remove debris greater than about 50mm and should always be used if there is a risk of damage to processing plant by large items.

Trommels

Trommels are used to remove rocks or trash in the range 10-100mm. Difficulty has been reported with the formation of clay balls on trommel screens, effectively trapping particles that are desired to pass through the device. A water spray can mitigate this problem.

Vibrating screens

These are used to make separations with particles in the range 4.0 – 0.1mm. Hydrocyclones overlap with this range and may be cheaper to run. Vibrating screens may be the better choice if there are variable feed rates, low volume, a wide variety of particle densities, or the feed solids content is greater than about 25-30%

Mechanical classifiers

Mechanical classifiers such as spiral or rake classifiers also operate in the same range as hydrocyclones. One might be selected for sand silt separation when a high solids content is required (eg when it is to be transported by a belt conveyor). They require a constant feed rate for reliable performance.

3.1.2.3 Hydrocyclones

One of the most established forms of processing is the use of the hydrocyclone, based on the fact that most contaminants are associated with the fine fraction (i.e. < 0.063mm) of dredged material. Hydrocyclones have wide use in the sand gravel and mineral processing industries. Their primary use is for separating different density or weight materials within a slurry mixture. Once the fine and coarse fractions have been separated, the fine fraction can be treated with some method appropriate to the contaminant (eg aeration in a basin) and the coarse fraction can be put to some beneficial use. If the coarse material is still contaminated with, for example, organic micropollutants, chemical extraction using triethylamine may be effective. PAH's may be removed by biodegradation when the contaminants are not too strongly absorbed to sediment particles (Van Dillen, 1991).

Several hydrocyclones are in constant use. For example the Port of Hamburg processes about 1 million m^3/year of sediment dredged from the River Elbe. The sediment contains about 50% sand (Detzner et al, 1998). A detailed account of the Hamburg treatment plant, MEHTA, is given in the project reports in Appendix 2.

Operation of the hydrocyclone is based on the principal of centrifugal force. It has no moving parts and requires relatively low energy to perform its primary function. The technique has been used in some European ports to increase solids concentrations in dredged slurries. The figure below illustrates a typical hydrocyclone. A slurry mixture is introduced to the feed chamber under pressure. The tangential entry causes the slurry to rotate at a high angular velocity, forcing coarser or heavier particles to the side walls where they continue downward with increasing velocity to the bottom of the cone section. This material then exits through the apex as a denser, higher percent solids, material, called the underflow. The cyclonic flow creates a centrally located low pressure vortex where the lighter, finer grained sediments and water flows upward and exits the top through the vortex finder. This finer grained, reduced percent solids slurry is called the overflow.

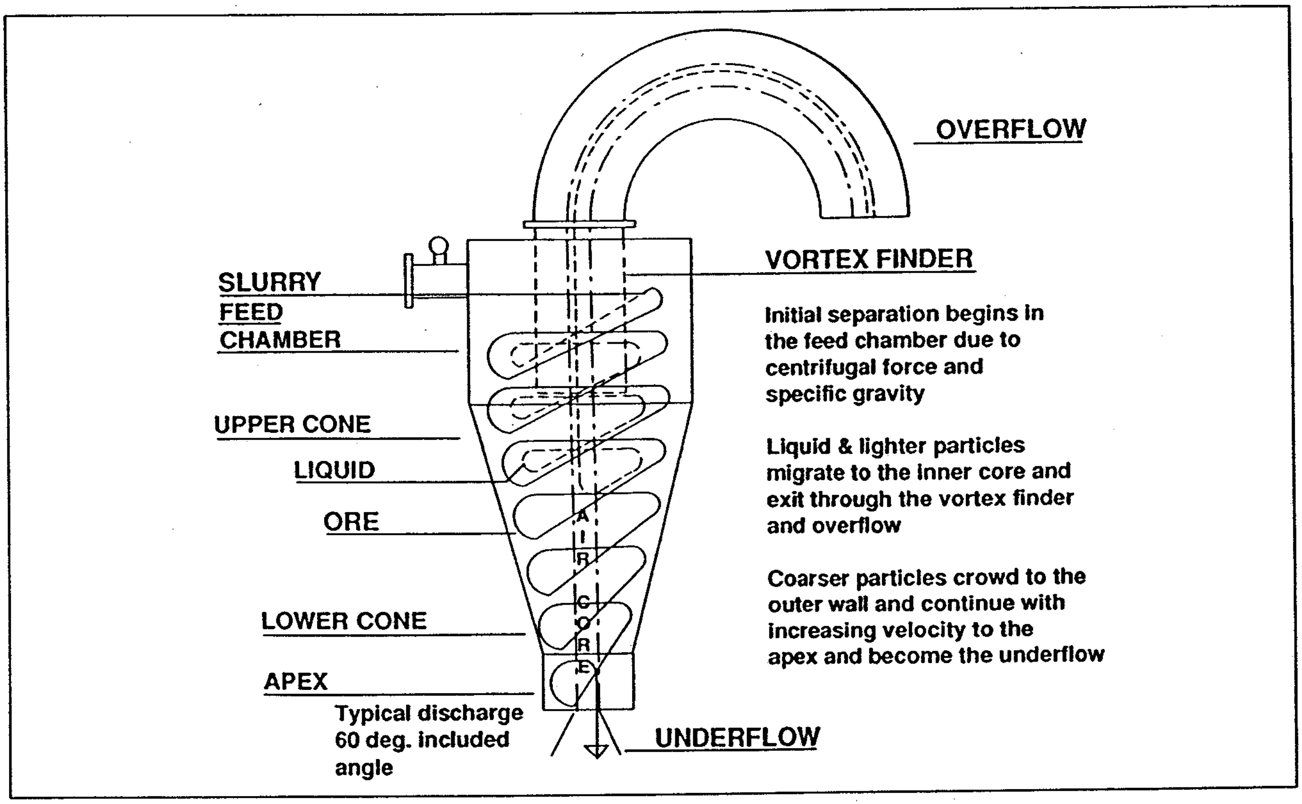


Figure 3.3 Hydrocyclone

A desired separation and production rate can be achieved by carefully designing the required hydrocyclone system to include suitable size devices. Table 3.4 provides examples of hydrocyclone sizes, defined by the diameter of the feed chamber, and associated operational characteristics. As indicated, typical size devices can rang from 0.76 - 0.91m with respective capacities ranging from 0.3 - 252.4 l/s

Table 3.4 Hydrocyclone size and capacity (Heibel et al 1994)

Size (m)	Capacity (l/s)	Inlet pressure (kPa)	Separation Size (micron)
0.076	0.3 - 2.2	68.9 - 482.6	10 – 40
0.102	1.3 - 5.7	68.9 - 413.7	10 – 40
0.152	2.5 - 12.6	68.9 - 344.7	15 – 40
0.203	5.7 - 18.9	34.5 - 275.8	20 – 44
0.305	12.6 - 50.5	34.5 - 206.8	30 – 44
0.457	18.9 - 94.6	34.5 - 179.3	44 – 53
0.610	50.5 - 151.4	34.5 - 172.4	53 – 74
0.762	94.6 - 220.8	34.5 - 172.4	74 – 100
0/914	113.6 - 252.4	34.5 - 137.9	100 – 149

Operationally hydrocyclones function efficiently with slurry concentrations of about 20% solids by weight. A properly designed device can be run anywhere from about 5% to 50% solids. It operates best at constant pressure and flow rate. They can be stacked in parallel to achieve higher production rates if necessary. For example to handle the discharge from a dredger with a 0.61m discharge pipe would require about 20 hydrocyclones in parallel, each having a 0.61m diameter inlet. It should be technically feasible to mount this number on a floating barge or mobile shore-based trailer.

Another advantage of the hydrocyclone is that it can be transported to the site. An example of the use of a portable hydrocyclone was the remediation of a 500m stretch of the Willemsvaart canal, Netherlands. The sediment was particularly contaminated with chromium and mineral oil with elevated concentrations of cadmium, arsenic, zinc, lead, EOX and PAH.

In total 16,208m^3 of sludge was mechanically dredged up, separated by hydrocyclone and dewatered (pressure belt filtration) in the mobile plant. In total, 8222m^3 of sand was separated and reused as category 1 building material and 8609 tonnes of residue were dumped on a landfill (Grinwis et al 1997).

3.1.2.4 Gravity separation

Gravity separators separate particles based on differences in their density. Organic contamination in sediments is often associated with solid organic material or detritus, which have much lower densities than the natural mineral particles of the sediment. Particles with high concentrations of heavy metals are significantly more dense than natural mineral particles. A dense media separator is used to facilitate the process of differential settling. A dense media separator was used at the ARCS Program demonstration at Saginaw (USACE Detroit, 1994), and at the demonstration conducted in Toronto, Ontario (Toronto Harbour Commission, 1993).

The traditional method for evaluating its suitability for a particular application is the "sink-float" test, using a variety of dense liquids such as bromochloromethane and tetrabromoethane (Mills, 1985). A sediment sample can be separated into fractions of differing specific gravity using these liquids and specially constructed funnels. These heavy liquids are suitable for isolating sediment which has metals attached. Density separations of organic contaminants can be predicted using water elutriation in which closely sized material is allowed to settle against a rising current of water.

A density based separation may be successful if contamination is found to reside disproportionately in a phase of different specific gravity than the bulk sediment matrix. For example, organic contaminants are often found attached to detrital material such as wood and leaves which have a much lower density than sediment. Most metallic phases are much more dense than sediment and can also be recovered. A specific gravity difference of 0.4 is usually sufficient to effect a separation by this method.

3.1.2.5 Froth flotation

Flotation can be useful to decontaminate polluted silt because:

- Many organic pollutants are naturally hydrophobic and are easy to float;
- Heavy metals, in particulate form, can be floated if the particles are hydrophobic;
- Flotation is already in use to clean up contaminated soils (Rulkens, 1985),
- The technique is capable of handling large volumes in relatively small installations;
- It is already well developed in the mining industry.

Compared with some other treatment techniques:

- Flotation is as fast and rugged as hydrocycloning, but it is more selective and the concentrate volume can be smaller. On the other hand chemicals have to be added;
- Flotation is faster than a biological treatment for organic contaminants and it needs smaller installations;
- Flotation needs less chemical reagents than acid leaching or complexation, because only the surfaces of the contaminants are involved. It is also not necessary to dewater all of the silt by a separate process. On the down side, the chemical conditions for a flotation are far more difficult to achieve (Dekeyzer et al, 1991).

Froth flotation is an advanced separation technique that is based on the chemical and physical characteristics of the contaminated sediment particles. Special frothing chemicals are added to the contaminated dredged material and the mixture has air forced through it. The froth that forms floats the contaminants (both metals and organics) away from the solid particles. Usually the very finest particles also float with the froth and become part of the contaminated fraction (PIANC 1996).

The technique is used in the mining industry to process millions of tonnes of ore per day. Copper, iron, phosphates, coal and potash are a few examples of materials that can be economically concentrated using this process. The process is based on manipulating the surface properties of minerals with reagents so that the mineral of interest has a hydrophobic surface (i.e. lacks affinity for water) such as wax. The minerals to be rejected have, or are made to have, a hydrophilic surface (i.e.. strong affinity for water). When air bubbles are introduced the hydrophobic minerals attach themselves to the bubbles and are carried to the surface and skimmed away.

When using flotation to remove oily contaminants from sediments, a surfactant is used in a manner that resembles a detergent. Most organic contaminants are naturally hydrophobic, and the objective in using a surfactant is to reduce the hydrophobicity of the oil phase to the point where it will be wetted by the water phase and detach itself from solid surfaces. Surfactants are able to accomplish this because such molecules have a lupophilic (fat soluble) head, which is absorbed into the oil phase, and a hydrophilic tail, which extends into the water phase. The result of this is that the overall hydrophobicity of the oil phase is decreased. The strength of a surfactant's attachment to an oil phases is approximated by the hydrophile-lipophile balance of the surfactant. Once freed of the solid surface, an oil droplet is assisted to the surface by air bubbles and skimmed away.

3.1.2.6 Magnetic separation

Magnetic separators are classified as two types depending on the intensity of magnetic field deployed (or the magnetic susceptibility of the minerals to be separated). Low-intensity separations usually employ permanent magnets and are most often used for material coarser than about 0.075mm with high magnetic susceptibility, such as iron ore. High-intensity separations that employ electromagnets are much more versatile and capable of recovering iron-stained or rusted silicate minerals from other purer, non-magnetic phases.

Wet, high-intensity magnetic separation (WHIMS) appears to be most applicable to sediment remediation with separations possible down to 0.005mm, although at very low capacity. The WHIMS unit is essentially a large solenoid. Magnetic material is trapped on the magnetised media in the chamber of the device, then flushed free in a rinse cycle when the feeding of sediment and magnetic current are stopped. Thus the WHIMS is a batch process rather than a continuous one (Bronkala, 1980).

Magnetic separation was used during part of the dredging and treatment demonstration conducted with sediments from the Welland River, Ontario (Acres International, 1993).

With the development of superconductivity the possibility to obtain sufficiently high magnetic fields in great volume makes it possible to increase capacity and selectivity of magnetic removal. A new type of separator (VGMS – volume gradient magnetic separation) was developed in Russia in which the working is free from the usual ferromagnetic elements and a non-uniform magnetic field is generated by an external magnetic system (Borzov et al, 1991).

The only practical way of evaluating feasibility is to carry out laboratory scale tests on samples of the actual sediment.

3.1.2.8 Sedimentation lagoons

An attractive alternative to costly processing plant is the use of sedimentation lagoons. These have received much attention in recent times. Whilst the practice of placing material in lagoons has not been primarily for the purpose of separation it was observed that separation did take place. Some tests were run to investigate this principle, eg van Mieghem (1991) and Deibel (1995). A handbook has been compiled (van Veen et al, 1996) for the application of the technique. Further tests are in progress.

The logistics have been considered by Cuperus et al (1997a). A separation depot is interesting because the material can be processed directly and continuously. The separation depot can both be used as a stand-alone technique and a treatment set in a larger process. The depot can furthermore be used for the dewatering of the dredged material (Section 3.1.1).

The surface area required for separation is 1m^2 per 1.5 to 3m^3 dredged material. Slightly over 40% of this area is required for storage. The number of m3 to be processed per m2 is influenced by the height of the depot and the throughput capacity required.

Intermediate storage is not necessary, which saves costs.

3.2 Treatment technologies

3.2.1 Basic approaches

Sediment that requires decontamination or detoxification may be treated using one or more of a number of physical, chemical or biological treatment technologies. These technologies aim to:

- Reduce contaminant concentrations to a target level; or
- Reduce contaminant mobility; or
- Reduce toxicity.

The means of achieving these are:
Destroying the contaminants or converting them to something less toxic;
Separating or extracting the contaminants form the sediment solids;
Reducing the volume of contaminated material by separation of cleaner particles from particles with a greater affinity for the contaminants;

Physically and/or chemically stabilising the contaminants in the dredged material so that the contaminants are fixed to the solids and are resistant to losses by leaching, erosion, volatilisation or other environmental pathways.

The main classes of treatment technology are:
- Thermal destruction
- Thermal desorption
- Immobilisation
- Extraction
- Chemical
- Biological
- Electrokinetic

These are described in detail in the following sections

3.2.2 Thermal destruction

The processes considered in this section are those that heat the sediment to very high temperature. They are generally the most effective for destroying organic contaminants but are also the most expensive. Included in this category are:
- Incineration;
- Pyrolysis;
- High pressure oxidation;
- Vitrification.

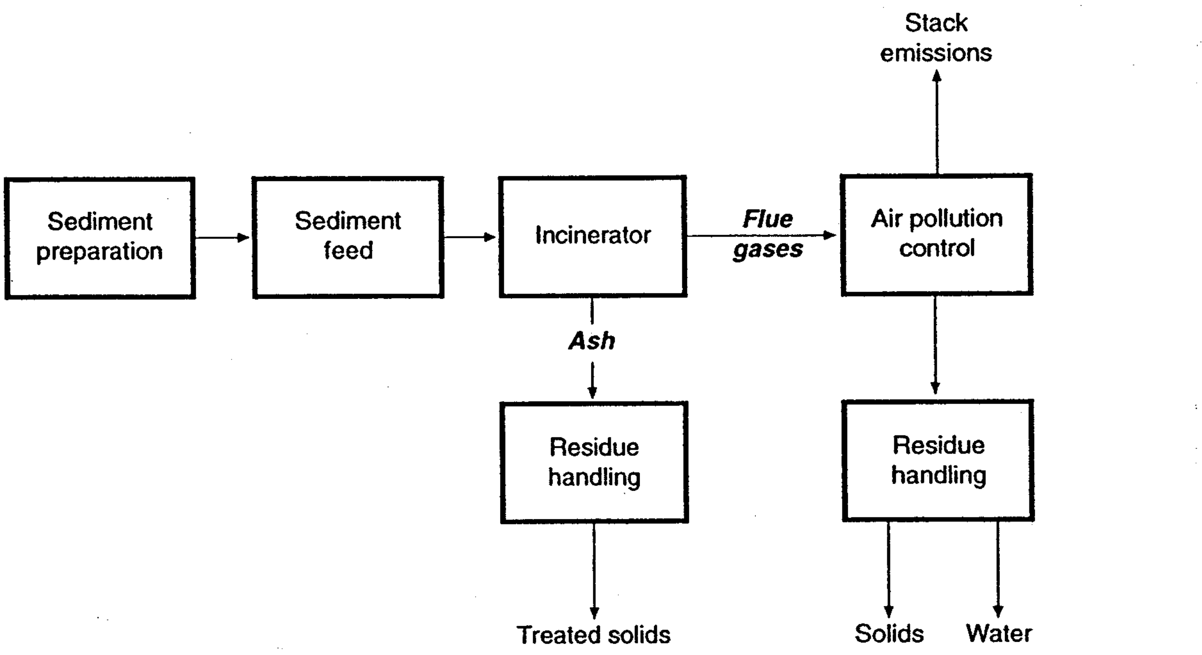
All organic compounds have boiling points or disintegrate below 850^0C. From experience with thermal treatment of contaminated soil it is known that temperatures between 500 and 600^0C are sufficient to obtain removal efficiencies of more than 99% for organic contaminants. At these temperatures heavy metals are not removed, with the exception of mercury, which has a boiling point of 357^0C and mercuric chloride (304^0C)

Most thermal technologies are highly effective at destroying a wide variety of organic compounds, including PCB's, PAH's, chlorinated dioxins and furans, petroleum hydrocarbons and pesticides. Whilst they do not destroy metals vitrification may immobilise them in a glassy matrix. Because volatile metals, particularly mercury, will tend to be released into flue gas, additional equipment may be required for emission control.

3.2.2.1 Incineration

Incineration is an established technique for hazardous waste, soil and contaminated dredged material. Because the energy requirement is high the costs are also tend to the highest of the treatment options.

Incineration is the most widely used process for destroying organic compounds in industrial wastes. It involves heating the sediments in the presence of oxygen to burn or oxidise organic materials, including organic compounds. Emission control is a critical part of the process. The basic process is described in the following diagram.



Source: USEPA (1990f)

Figure 3.4 **Incineration process**

Application of incineration to wet solids such as sediments is uncommon: all traces of moisture must be driven off before the solids will burn. This requires expensive dewatering and drying as described in Section 3.1.1. Incineration tends to be a controversial issue in local communities.

Incineration does not remove metal contamination. In fact most incineration processes increase leachability of metals through the process of oxidation (exceptions include the slagging or vitrifying technologies which produce a nonleachable, basalt like residue. This leachability can be used to advantage if the residue is treated using a metal extraction process. In the US the leachability of metals is generally measured using the toxicity characteristic leaching procedure (TCLP) test. Incinerator ash that fails this test must be disposed of as hazardous waste.

Incineration technologies can be divided into two categories: conventional and innovative. Because gaseous emissions from incinerators present a potentially large contaminant loss pathway, the emission control system is a critical component for both. Conventional technologies include rotary kiln, fluidised bed, multiple hearth, and infrared incineration. They are listed in Table 3.5. They typically heat the feed materials to between 650 – 980^{0}C. An afterburner or secondary combustion chamber is generally required to achieve complete destruction of the volatilised organic compounds. All the processes produce a dry ash residue.

Table 3.5 Summary of conventional incineration technologies

Technology	Description
Rotary Kiln Incineration	Consists of a solid feed system, primary combustion chamber, an inclined rotating refractory-lined cylinder, an afterburner, and air pollution control unit and a process stack. Temperatures range from 650 – 980^{0}C with a retention time in the range 15 mins – several hours. The secondary chamber reaches temperatures of 1300^{0}C with a retention time of 2 seconds.
Fluidised bed incineration	Consists of a cylindrical, vertical, refractory-lined vessel containing inert granular material (sand) on a perforated metal plate. Combustion air is introduced at the bottom of the incinerator causing bedding material to become fluidised. Temperatures range from 760 – 870^{0}C. Exhaust gases and volatile compounds pass into a secondary combustion chamber where the retention time is about 2 seconds.
Multiple heart incineration	Consists of a refractory, steel lined shell, a rotating central shaft, a series of solid flat hearths, a series of rabble arms with teeth for each hearth, an air blower, waste feeding and ash removal systems and fuel burners mounted on the walls. Temperatures range from 760 – 980^{0}C.
Infrared (SHIRCO) incineration	Consists of a waste preparation system and weigh hopper, an infrared primary combustion chamber, a propane-fired afterburner, emission control systems and a process management and monitoring control centre. Temperatures reach up to 1010^{0}C with retention times of 10 – 180 minutes in the primary combustion chamber. Afterburner temperatures range from 1200 – 1300^{0}C.

There are a number of innovative processes that are designed specifically for hazardous and toxic wastes: these are proprietary systems and are listed in Appendix 2. Generally they operate at higher temperatures and achieve greater destruction and removal efficiencies. Most produce a dense slag or vitrified solid rather than a free-flowing ash. They tend to be very expensive but offer the advantage of producing a non-leachable residue.

3.2.2.2 Pyrolysis (also known as thermal reduction)

A relatively new type of thermal treatment is Pyrolysis or thermal reduction. In this technique, temperatures as high as those used in incineration are used but a gas other than oxygen (usually hydrogen) is present in the reactor. The result is the reduction of organic molecules into lighter and less toxic products (PIANC, 1996).

A pyrolysis system consists of a primary combustion chamber, a secondary combustion chamber and pollution control devices. High temperatures, 540 – 760^{0}C, cause large, complex molecules to decompose into simpler ones. The resulting gaseous product can be collected (eg on a carbon bed) or destroyed in an afterburner at 1200^{0}C. A summary of proprietary technologies is given in Appendix 2.

The Thermal Gas Phase Reduction Process is a specialised version in which a reducing agent (hydrogen gas) is introduced to remove chlorine atoms from PCB's or dioxins. It was shown to give extremely high destruction efficiencies with Hamilton sediment (ELI, 1992). It was further tested under the Superfund Evaluation Program (SITE) with PCB contaminated soil (USEPA 1994b).

Pyrometallurgy, or smelting/calcination, is a non-proprietary form of pyrolysis. It is generally used to treat metal bearing ores. High levels of metals or metal oxides can be recovered from waste materials of similar metal content because the effectiveness of recovery is directly proportional to the metal content of the waste. However, this process has the potential for forming toxic sludges and is expensive (Averett et al, in prep).

A method has been developed to remove amphoteric elements like arsenic, phosphorous, chromium, aluminium and others from sediments. Thermal treatment at 900^{0}C in the presence of alkaline reagents, like soda, converts the insoluble amphoterics into their soluble sodium salts, which can be easily extracted. The amphoterics are finally fixed as calcium salts in the form of pellets. The solids remaining after extraction are more amenable for re-use or further treatment. The whole process does not result in additional liquid waste that cannot be re-used. The efficiency of removal was demonstrated to be 90% or more (Van Breemen and Koreman, 1991).

3.2.2.3 High-pressure oxidation

This category includes two related technologies, wet air oxidation and supercritical water oxidation. Both use the combination of high temperature and pressure to break down organic compounds. Typical operating conditions for both processes are shown in Table 3.6 below. This shows that wet air oxidation can operate at pressures one-tenth of those used during supercritical water oxidation.

Table 3.6 Operating conditions for high pressure oxidation processes (USEPA, 1991: Kiang and Metry, 1982)

Process	**Operating temperature ^{0}C**	**Operating pressure MPa**
Wet air oxidation	150-300	2,000-20,000
Supercritical water oxidation	400-600	22,300

Wet air oxidation

Wet air oxidation is a commercially proven technology, although its use has generally been limited to conditioning of municipal wastewater sludges. The technology can degrade hydrocarbons (including PAH's) some pesticides, phenolic compounds, cyanides, and other organic compounds (USEPA, 1987b). However, destruction of halogenated organic compounds (eg PCB's) with this process is poor. In bench-scale tests on Indiana Harbour sediments it was found that only 35% of influent PCB's were destroyed. It may be possible to improve oxidation through the use of catalysts (Averett et al, in prep).

Wet oxidation is a chemico-physical process operated by adding oxygen at elevated temperature and pressure which aids in the oxidation of organic compounds (Rienks, 1996). For example, phenol is oxidised in the gas phase starting at 1000^{0}C, whereas in the liquid phase it starts at 200^{0}C. The pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phases at the operating temperature. The reaction must take place in the aqueous phase because the chemical reactions involve both oxygen (oxidation) and water (hydrolysis). Wet oxidation processes involve a number of reactions in series, which are not exactly elucidated because of its complexity. The generally accepted theory describes the reactions by means of free radical-mechanisms. The two most important controllable factors to increase oxidation rates are reaction temperature and the use of catalysts. Two processes are described, VerTech and Bayer Loprox.

The VerTech process uses a vertical sub-surface oxidation vessel with a length of 1280m. The reactor consists of two concentric tubes, the downcomer (dia 0.2m) and the riser (dia 0.34m). Oxygen is injected in the downcomer by two separate pipes (each 0.06m dia). For heat exchange distilled water is pumped through a third pipe that surrounds the riser. The reactor is placed in a cemented borehole into the subsurface. Pressure is built up by the hydrostatic head, about 10 MPa in the reaction area at the bottom of the reactor. Reaction temperature depends on the type of sediment to be treated and may be varied by means of the heat exchanger. Typically reaction temperatures near the bottom are between 200 and 300^{0}C.

The advantages of this type of reactor are:
- An ideal plug flow regime for a high performance;
- An efficient heat exchange along the reactor length;
- A lighter construction compared to surface wet oxidation techniques.

In 1995, 710 m3 fine fraction of harbour sediment, contaminated with PAH (16 EPA) and mineral oil, was treated in the full scale operational VerTech plant for treating sewage sludge. The plant is situated in Apeldoorn, The Netherlands. Results of the test corresponded with earlier laboratory test results. PAH degradation was more than 98% (sum PAH 16 EPA <0.05 mg/kg dry solids). Mineral oil was not completely oxidised but was decomposed into small chain oil fractions. Additional landfarming resulted within 8 weeks in complete degradation (<20 mg/kg ds). The characteristics of the resulting residue cake was thought to be possibly suitable for use in civil engineering works (Rienks, 1996). Unfortunately due to incomplete oil removal and too high a zinc content this turned out to be not possible (Rienks 1997).

The Bayer Loprox process consists of an upflow operated bubble column reactor. The process is operated at temperatures below 200^{0}C and pressure below 2 MPa. The reactor is pressurised with injector pumps. Reaction rate is catalysed by adding Fenton's reactant, a combination of divalent iron and quinone, or adding only divalent iron. This catalytic oxidation shows optimal results under acid conditions, about pH 2.

The advantages of wet oxidation processes are:
- High destruction efficiencies;
- Low energy consumption;
- Dewatering before treatment is not necessary;
- The treated material has excellent soil mechanical properties;
- Large treatment capacities are possible on a small area.

Supercritical water oxidation

An important characteristic is the critical point of water, which divides the operational conditions into subcritical and supercritical wet oxidation. This point is reached at a pressure of 22.1 MPa and a temperature of 374^{0}C. Above this point there is no physical difference between liquid and gas, all organic compounds are solved very well, whereas inorganic compounds precipitate as salts. Supercritical wet oxidation has not reached full scale application, mainly because of reactor material problems (corrosion) (Rienks, 1996).

The supercritical water oxidation process is relatively new and has only been tested at bench scale. Available data have shown essentially complete destruction of PCB's and other stable compounds.

3.2.2.4 Eco Logic destructor

The Eco Logic destructor was tested on bench scale (Rienks, 1997). The desorption unit consisted of a molten tin bath at 550 – 600^{0}C. The vapours were treated with hydrogen atmosphere at 850 – 900^{0}C. The removal of mercury, hexachlorobenzene, polychlorobifenyls, furans and dioxins amounted to more than 90-95%. The destruction efficiencies for the organic compounds amounted to 92-99%. However, the treated sediment was contaminated with tin and estimated treatment costs were too high to consider further experiments.

3.2.2.5 Vitrification

This is an emerging technology that uses heat to destroy organic compounds and immobilise inert contaminants. This is a thermal process that is essentially a thermal desorber for the organic contaminants and mercury but also immobilises metal. The process is run at a high enough temperature to melt the silica and metals in the contaminated dredged material. After cooling the material is turned into a hard slag-like product from which the metals will not leach. Most technologies produce a product such as gravel or bricks that can be used as a building material. A disadvantage is the high energy consumption and flue gas emission (PIANC 1996).

Dutch tests

Two concepts were studied under the Netherlands DPTP programme:

- Sintering of pelletised mud at approximately 1200°C to produce artificial gravel;
- Melting at 1200 – 15000C followed by cooling into a glass slag (vitrification) or slow cooling to crystallize into a stone product (basalt).

Both sintered gravel and molten products meet Dutch environmental and construction standards.

Tests carried out in the Netherlands are described in Schotel et al (1996).
About 1500m^3 was processed by sieving and hydrocycloning to separate the sand and the fines. The latter were dewaterd by filterbelt press as described in Section 3.1. The clean sand was ready for recycling, leaving a heavily contaminated sludge cake. The moisture content was lowered by drying the material in two rotary kilns at 100°C and 300°C with residence times of 6 and 10 minutes respectively. Organic components are partly pyrolised during this process. Dust from the flue gases is collected in a cyclone and returned to the dried material. Flue gas treatment is necessary, especially for mercury. The dried product has a dry solids content of over 95% and is collected in large bags.

The next stage of the process is melting at 1400°C after mixing with about 10% additives (Ca and Mg) to improve product quality. The plant used is a Contop smelting cyclone situated neat Winterberg in Germany. Melting is done at reducing conditions to remove more than 95% of zinc, lead, cadmium, arsenic, and antimony. The other heavy metals are immobilised as oxides in the slag. Flue dust with an estimated metal content of 10-25% can be re-melted to a marketable ore-product.

Next is the cooling process, where the cooling rate determines the degree of crystalisation. Cooling of the melt results in glass slags, which are crushed into a granulate, with a basaltic composition. Slow cooling in moulds in a specially designed batch oven should result in hexagonal blocks with a crystalline structure and a basaltic composition.

Two types of material are produced: approximately 275 tonnes of granulate and approximately 25 tonnes of blocks. The products were analysed for chemical composition and leaching performance to check if the environmental standards for use as building materials are met (Category 1 of the Dutch Regulations of Building Materials).

Granulate can be used in concrete and asphalt, while blocks are meant for dyke construction.

Further development work was carried out by Heijmans Milieutechniek, Gemco Engineers and Techno Invent (Bolk et al 1997). They developed a method based on thermal immobilisation to produce high quality building material from, among others, highly contaminated sediments. The main steps in the process are:

- Pretreatment (removal of sand fraction and dewatering);
- Thermal drying;
- Smelting at 1400 – 1500°C with an adequate residence time. The plant consists of a furnace heated by oxy-fuel burners and the feed is introduced tangentially by pneumatic transport. The use of oxygen enables the furnace to run under reducing atmosphere whilst maintaining the required temperature.

This causes the bulk of the volatile contaminants (zinc, lead, cadmium, arsenic and antimony) to report to the furnace gas. The gas is subsequently cooled and cleaned in a radiation chamber, a bag filter and an activated carbon guardbed. In this system the volatilised contaminants concentrate in the bag filter dust;

- Adding fluxes in order to tune the feed composition to the desired range of basaltic rock and to improve slag behaviour to facilitate the operation of the furnace (to reduce costs certain waste materials can be used , eg. asbestos as a source of magnesium); To produce granular material moulds with a content of about 200 kg pf slag are used.
- Cooling down the slag under controlled conditions so that a crystalline structure similar to natural basalt is achieved. Subsequent crushing a sieving of the slag blocks produces granular material to the desired grading. Shaped products can also be made by using steel moulds.

Organic contaminants are totally destroyed in the process. Heavy metals are separated to an extent that they are useful to the metallurgical industry and the remainder are strongly bound in the crystal structure. By using sediment sludge and/or residue from soil decontamination as mineral basis flow, other complex contaminated waste flows can be incorporated, having a positive effect on the economic feasibility.

The pilot scale tests successfully treated 300 tonnes of material. The system is thought to have full scale commercial potential.

Development in the USA

The US has developed a process using electrical energy to produce the necessary temperatures for vitrification (USEPA, 1994). A typical unit consists of a reaction chamber divided into two section: the upper section introduces the feed material containing bases and pyrolysis products, while the lower section contains a two-layer molten zone for the metal and siliceous components of the waste. Wastes are vitrified by passing high electrical currents through the material. Electrodes are inserted into the waste solids and graphite is applied to the surface to enhance its electrical conductivity. A large current is applied, resulting in rapid heating of the solids and causing the siliceous components of the material to melt. The end product is a solid, glass-like material that is very resistant to leaching. Temperatures of about 1600^0C are typically achieved.

Vitrification units have been demonstrated in pilot scale and full scale.

In-situ vitrification is a patented thermal destruction technology developed by the Battelle Memorial Institute's Pacific North West Laboratory. Although it was designed for contaminated soils it could presumably be adapted for dredged material.

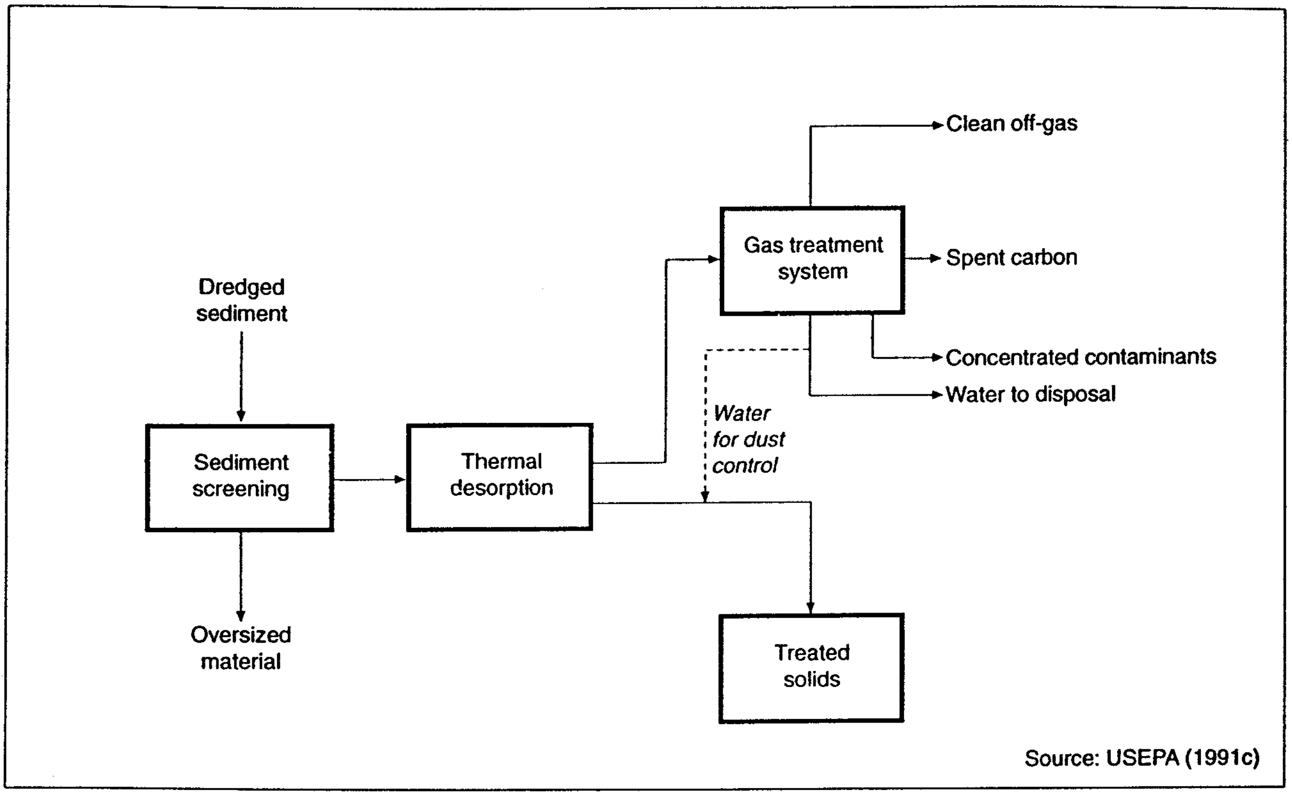
Table 3.7 Summary of thermal destruction technologies (After USEPA, 1994)

Technology	Advantages	Disadvantages
Conventional Incineration	Can process large waste volumes. Proven commercially at full scale portable equipment. Widely available. Can achieve >99.99% destruction of organic compounds. Applicable to a wide variety of compounds.	Generates large volumes of exhaust gas that must be treated. Can volatilise metals, especially mercury. Increases leachability of metal in treated solids. Public opposition is usually high. Can produce chlorinated dioxins and furans. Extensive pretreatment (drying and screening) may be required.
Innovative incineration	Can achieve greater destruction and removal efficiencies.	Most technologies still in development stage.

	Most processes produce an inert slag which is resistant to leaching.	Extensive pretreatment may be required. More expensive than conventional incineration. Public opposition likely. Can produce chlorinated dioxins and furans.
Pyrolysis	Can achieve greater destruction and removal efficiencies that conventional incineration. Can produce inert slag.	Most technologies still in development stage. Extensive pretreatment may be required. More expensive than conventional methods.
High pressure oxidation	Does not require dewatering and drying of sediments. Costs less than incineration. Supercritical water oxidation effective for many types of organic compounds, including polychlorinated biphenyls.	Wet air oxidation not effective for polychlorinated biphenyls and other chlorinated organic compounds. Supercritical water oxidation is still in the development stage.
Vitrification	Produces an inert glass/slag that is resistant to leaching.	Most technologies still in the development stage. More expensive than incineration. Not feasible for sediments containing high levels of electrically conducting metals. Molten product may take months to years to cool.

3.2.3 Thermal desorption technologies

Thermal desorption physically separates volatile and semi-volatile compounds from sediments by heating the sediment to temperatures ranging from 90 – 540^{0}C. Water, organic compounds and some volatile metals are vaporised by the heating process and are subsequently condensed and collected as liquid, captured on activated carbon and/or destroyed in an afterburner. An inert atmosphere is usually maintained in the heating step to minimise oxidation of organic compounds and to avoid the formation of compounds such as dioxins and furans. A typical process is shown in Figure 3.5.



Source: USEPA (1991c)

Figure 3.5 Thermal desorption process

The temperature of the sediment in the desorption unit and the retention time are the most significant factors affecting performance. Heating may be accomplished by indirectly fired rotary kilns, heated screw conveyors, a series of externally heated distillation chambers or fluidised beds.

Thermal desorption processes offer several advantage over thermal destructive processes, including:
- Reduced energy requirements;
- Less potential for formation of toxic emissions;
- Smaller volumes of gaseous emissions.

The disadvantages include:
- The need for a follow-on destruction process for the volatilised organic compounds;
- Reduced effectiveness for less volatile organic compounds.

The factors that affect the efficiency are shown in the following table.

Table 3.8 Factors affecting thermal desorption processes After USEPA (1988, 1991c)

Factor	Effect
Sediment type	High concentrations of clay or silt increase fugitive dust emissions after processing; Cohesive clays may clump into aggregates that reduce contaminant desorption effectiveness and result in caking. This may interfere with the operation of the process equipment.
Solids content	Low solids content increases the energy required to heat the sediment to desorption temperatures. Solids content should generally be greater than 40%.
Presence of volatile metals	Volatile metals (such as mercury) will volatilise during thermal desorption processing and must be captured by an emission control system.
pH <5, >11	Corrosive effect on equipment.
Operating temperature	Contaminants with higher boiling points require processes capable of achieving higher temperatures.
Particle size	Oversized particles must be screened out or reduced in size prior to processing. Maximum size is generally 50mm.
Contaminant flammability	An oxygen deficient atmosphere should be maintained during processing because of the risk of volatile compounds igniting when heated.

The following types of processor are considered:

- High temperature thermal processor;
- Low temperature thermal treatment system;
- XTRAX System;
- Desorption and vaporisation extraction system;
- Low temperature thermal aeration system;
- Anaerobic thermal processor systems.

A list of suppliers is given in Appendix 6.

3.2.3.1 High temperature thermal processor

The high temperature thermal processor (Remediation Technologies Inc. (ReTec)) uses a Holoflite dryer, a heated screw conveyor, to heat the sediment and drive off water vapours, organic compounds and other volatile compounds. The screws for the dryer are hated by a hot molten salt that circulates through the stems and blades of the augers and well as through the trough that houses the augers. The molten salt is a mixture of salts, primarily potassium nitrate. Maximum soil temperatures of 450^{0}C are attainable (USEPA, 1992). The motion of the screws mixes the sediment to improve heat transfer and conveys the sediment through the dryer. Off gases are controlled by cyclones, condensers and activated carbon. Removal efficiencies of 42-96% were achieved for PAH's in Buffalo River Sediments (USACE Buffalo District, 1993). Greater than 89% of PCB's were removed by a pilot unit from Ashtabula River sediments.

3.2.3.2 Low temperature thermal treatment system

This also uses a Holoflite dryer similar to the ReTec process. However the heating fluid is a thermal oil heated by a separate, gas-fired unit. The maximum temperature for the heating fluid (around 350^{0}C) is the limiting factor in this process. This allows the sediment to be heated to about 290^{0}C (Parker and Sisk, 1991); however, higher temperatures would likely be required to effectively remove PCB's from sediments.

Vapours from the contaminated material are passed through a particulate filter, scrubbers or condensers, and carbon adsorption columns, and may require additional post treatment. In demonstrations an afterburner was attached to the gas stream operating at temperatures as high as 1200^{0}C to destroy the organic compounds. Removal efficiencies >99% have been reported for PAH's (USEPA 1991). The capacity of the full-scale system is 6.8 tonnes/hour (Parker and Sisk, 1991).

3.2.3.3 X*TRAX System

The X*TRAX thermal desorption system (Chemical Waste Management) uses and externally fired rotary kiln to heat sediment to temperatures ranging from 90 – 480^{0}C. Water and organic compounds volatilised by the process are transported by a nitrogen carrier gas to the gas treatment system. First a high energy scrubber removes dust particles and 10-30% of the organic compounds. The gases are than cooled to condense most of the remaining vapours. About 90-95% of the cleaned gas is reheated and recycled to the kiln. The remaining 5-10% is passed through a particulate filter and activated carbon and is then released to the atmosphere (USEPA, 1992). Pretreatment requirements include screening or grinding to reduce particle size to less than 50mm. Post treatment includes treatment or disposal of the condensates and spent carbon. Removal efficiencies greater than 99% have been demonstrated for volatile organic compounds, pesticides and PCB's. USEPA (1992) reported that mercury, one of the more volatile metals, had been reduced from a soil concentration of 5100ppm to 1.3ppm using this process. While this system has been used for soils it has not been demonstrated for contaminated sediments.

3.2.3.4 Desorption and vaporisation extraction system (DAVES)

"DAVES" is a registered name for this process (Recycling Sciences International, Inc.) It uses a fluidised bed maintained at a temperature of about 160^{0}C and a concurrent flow of air from a gas fired heater at 540-760^{0}C. AS the contaminated material is fed to the dryer, water and contaminants are removed from the solids by contact with the hot air. Gases form the dryer are treated using cyclone separators and bag houses for removal of particulates and using a venturi scrubber, counter-current washer and carbon adsorption system for removal of water and organic compounds. On-site treatment of liquid residues is available as a part of the process. The mobile DAVES unit has a capacity of 10-66 tonnes/hour. It is applicable to most volatile and semivolatile organic compounds and PCB's (USEPA 1992). The process was tested with sediments from Waukegan Harbour, Illinois, with reported reductions in PCB concentrations from 250 ppm to <2 ppm (USEPA 1991c).

3.2.3.5 Low temperature thermal aeration system

The low temperature thermal aeration system (Canonie Environmental Service Corp) uses a direct-fired rotary dryer that can heat soil to temperatures of 430^{0}C. The gas stream from the dryer is treated for particulate removal in cyclones and/or baghouses. Organic compounds may be destroyed in an afterburner or scrubbed and adsorbed onto activated carbon. The full scale unit can process 11-15m^3/hour. Effective separation of volatile organic compounds and PAH's from contaminated soils has been demonstrated (USEPA, 1992).

3.2.3.6 Anaerobic thermal processor systems

The anaerobic thermal processor (ATP^R) system (SoilTech ATP Systems, Inc.) also known as the AOSTRA-Taciuk process, consists of four processing zones. Contaminated material is led into a preheat zone maintained at temperatures of 200-340^{0}C where steam and light organic compounds are separated from the solids. The solids then move into a 480-620^{0}C retort zone, which vaporises the heavier organic compounds and thermally cracks hydrocarbons, forming coke and low molecular weight gases. Coked solids pass to a combustion zone (650-790^{0}C). The final zone is a cooling zone for flue gases. The organic vapours are collected for particulate removal and for recovery or adsorption on activated carbon (USEPA, 1992). This system was used for clean-up of PCB contaminated sediments and soil from the Outboard Marine Corp. Superfund site in Waukegan Harbour, Illinois. A full scale unit rated at 23 tonnes/hour was used and produced PCB removals of 99.98% (Hutton and Shanks, 1992). Pretreatment is necessary to reduce the feed materials to less than 50mm diameter.

3.2.4 Immobilisation technologies

Immobilisation alters the physical and/or chemical characteristics of the sediment to reduce the potential for contaminants to be released from the sediment when placed in a disposal site. The principal contaminant loss pathway that is reduced is leaching from the disposal site to groundwater and/or surface water.

Thermal immobilisation (or vitrification) destroys organic material while immobilising inorganic materials. It thus falls into two categories of treatment, vitrification and Immobilisation. To avoid repetition the process is described in Section 3.2.2.4 under the heading of Vitrification.

Physical stabilisation processes improve the engineering properties of the sediment, such as compressive strength, bearing capacity, resistance to wear and erosion and permeability. Alteration of the physical character of the sediments to form a solid material (eg a cement matrix) reduces the accessibility of the contaminants to water and entraps or microencapsulates the contaminated solids within a stable matrix. Because most of the contaminants in dredged material are tightly bound to the particulate fraction, physical stabilisation is an important mechanism (Myers and Zappi, 1989). Solidification processes may also reduce contaminant losses by binding the free water in dredged material (a large contributor to the initial leachate volume in a disposal site) into a hydrated soil.

Chemical stabilisation is the alteration of the chemical form of the contaminants to make them resistant to aqueous leaching. S&S techniques are formulated to minimise the solubility of metals by controlling pH and alkalinity. Anions, which are more difficult to bind in insoluble compounds, may be immobilised by entrapment or microencapsulation. Chemical stabilisation of organic compounds may be possible but the mechanisms involved are not well understood (Myers and Zappi, 1989).

The distinction between physical and chemical stabilisation is not absolute. Cement based S&S is actually a chemical treatment in which the basic process occurring is the hydration of cement. This consumes water and thickens the mix.

The main disadvantage of immobilisation techniques, and the reason why many countries do not allow immobilised contaminated dredged material to be used in construction, is that the contaminants remain in the material. It is possible that the effectiveness of the immobilisation will be short term and that leaching of contaminants will occur after a number of years (PIANC 1996). However, techniques are improving and accelerated leaching test with MBS (see below) gave a more positive result.

3.2.4.1 Physical stabilisation (Solidification and Stabilisation (S&S))

The process

Binders used to immobilise contaminants in sediment or soils include cements, pozzolans and thermoplastics (Cullinane et al, 1986: Portland Cement Association, 1991). In many commercially available processes, proprietary reagents are added during the basic solidification process to improve the effectiveness of the overall process or to target specific contaminants.

The effectiveness of an immobilisation process for a particular sediment is difficult to predict and can only be evaluated using laboratory leaching tests. A diagram of the process is shown in Fig 3.6 below.

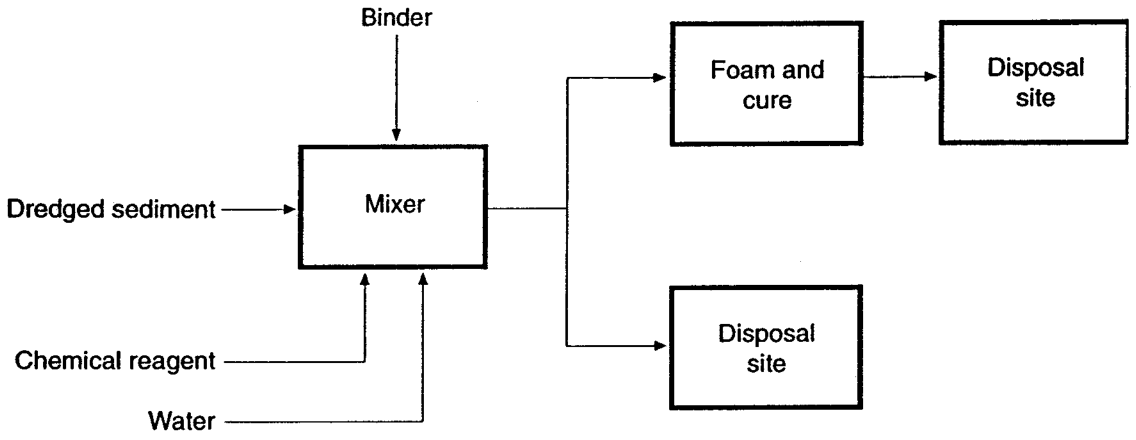


Figure 3.6 Immobilisation process

Immobilisation technologies have been evaluated for both freshwater and saltwater environments. The investigations carried out in the US showed that physical stabilisation of sediments is easily achieved using a variety of binders, including various proprietary processes. Leaching tests on the solidified solids showed mixed results; the mobility of some contaminants was reduced while the mobility of others increased. (Myers and Zappi, 1992). The ARCS Program evaluated solidification/stabilisation of Buffalo River sediments using three generic binders, Portland cement, lime-fly ash, and kiln dust. Leaching of lead, nickel and zinc was reduced by the cement process, but leachate concentrations of copper were significantly increased by the process (Fleming et al, 1991). A similar result was obtained in the production of "Mudcrete" in New Zealand (in Burt 1997).

The quality of the dredged material has an effect on the engineering properties of the product. For example researchers (Shin et al 1992, Diet 1996) suggest that while copper, lead and zinc inhibit the initial hardening of cement, cadmium, chromium and mercury have the opposite effect. The inhibition effect may result from a gelatinous and impermeable coating that forms around the major components and acts as a barrier to water.

<u>Newark project</u>

The Newark project in the USA is an example of an ex-situ stabilisation and solidification process, where direct cement addition and mixing is used to treat contaminated sediments. This project has been examined in some detail and is reported in Appendix 5. Thousands of cubic metres of sediment with low level organic and inorganic contamination are dredged daily from the Ports of New York and New Jersey. Barges are filled with sediment and are taken to a recycling facility in Port Newark.

The dredged material naturally has low cohesion and strength. However, stabilisation and solidification is being used to transform the chemical and physical properties of the material, creating an engineered structural fill. The mixing equipment is able to thoroughly blend a cement slurry within the barges and dewater the dredged sediments. The project is using some 20,000 tonnes of cement per week. It is anticipated that around 450,000 tonnes of cement will eventually be used. In excess of 40 million m^3 of dredged material is likely to be produced from the New York and New Jersey harbour channels.

The treated material is stockpiled before being transported by lorry a few miles to a reclamation site where it is spread and compacted. When completed the site will be used as a shopping mall, with a large adjacent parking lot. Further contracts are expected to be awarded using this process. Fortunately there is a considerable area of derelict ex Defence Department land available which can accommodate the treated silt. The land is nearly all earmarked for redevelopment.

The contractor has developed specialist (patented) mixing equipment which ensures that the cement slurry is blended efficiently with the dredged silt. Overall there will be a total of 1 to 2 M cu yards of dredged material "beneficially" used at this site.

In-pipe mixing in Japan

A variation on the Newark approach is to add the cement in the pipeline between the dredger and the disposal site, although the mixing has to be fairly near the disposal site end. In the example cited below, the material has been dredged by grab and placed in barges. The other interesting aspect is that the entire plant is mounted on a pontoon and can therefore be moved to other sites. The method is claimed by its Japanese inventors to reduce costs by about 15% compared to other mixing techniques (Sakamoto 1998). The method uses "plug flow" generated in the pipeline with compressed air assistance to mix cement based solidifier with mud in the pipeline. Uniform cement mixing is achieved by injecting solidifier into an expander pipe with a larger diameter than the pipeline. This method eliminates conventional mixing plant and will be more economical than other methods. Field tests were carried out in July 1997, injecting $50kg/m^3$ of solidifier in the expander pipe fitted with a 200m3/hour capacity pipeline. The system comprises the following four main elements:

1. Unloading section

Dredged mud is unloaded using the backhoe for discharge into the hopper. Potentially harmful items like rocks and wood are removed using vibration sieves. The mud is stored in the vessel beneath the sieve and an agitator, installed in the vessel, constantly supplies the mud to the mixing plant which fluidises the mud using a screw feeder.

2. Solidifier section

The solidifier is supplied by the screw feeder to the mixer in amounts measured by load cells. The supply of solidifier can be adjusted to meet the solidification purpose.

3. Mixing section

The dredged material and the solidifier are mixed uniformly by a double-axis paddle mixer. The mixer is the "tilting" type. The time necessary for mixing can be controlled.

4. Compressed air transfer section

The mixed, modified dredged material is stored in the vessel and supplied to the pressurised pump unit by the screw feeder to be pumped out through the transfer pipeline to the disposal site. Generally the addition of the solidifier increases the friction within the pipeline and thus limits the transfer distance to about 200m.

The solidifier injection is illustrated in the diagram below.

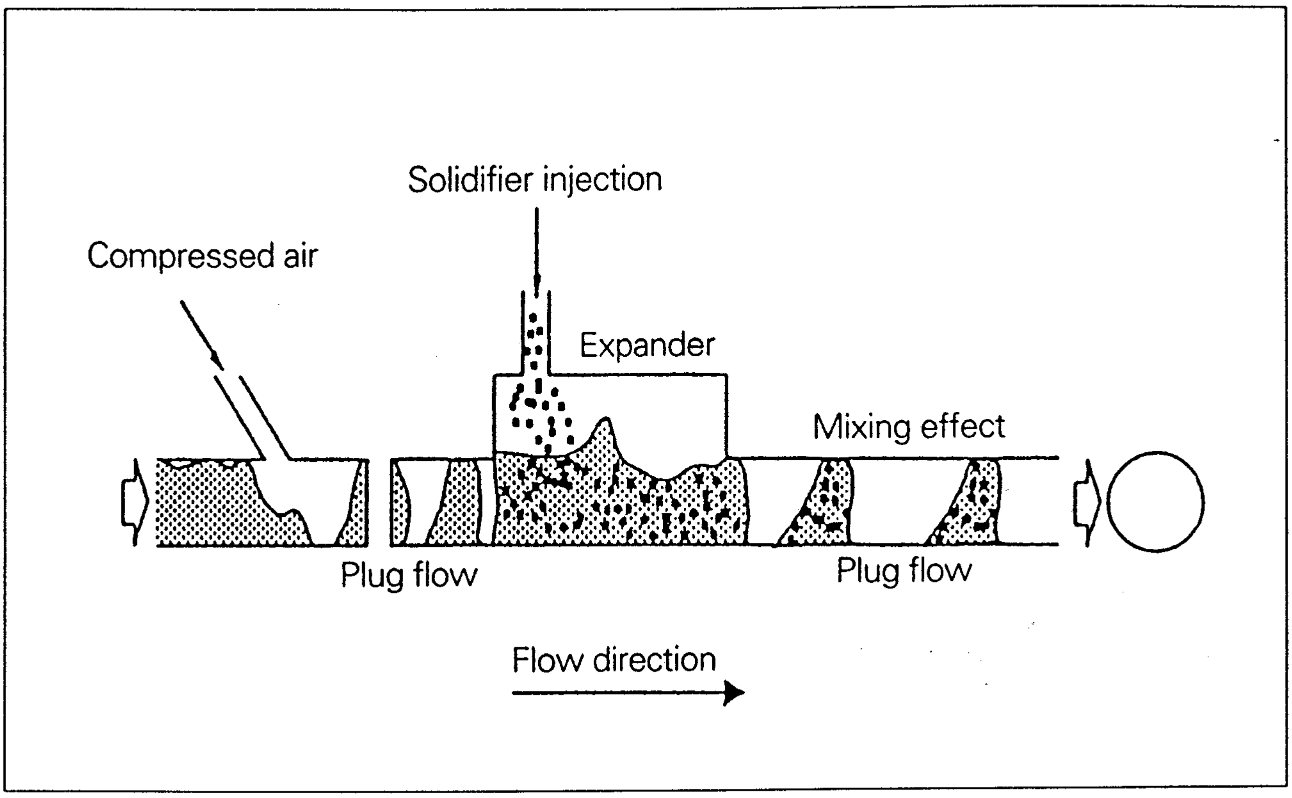


Figure 3.7 **Solidifier injection (Sakomoto 1998)**

French trials
Boutouil and Levacher (1997) report studies using different types of cement, lime and polymer (Le Gouevec 1996). The studies are a part of a research programme conducted by Le Laboratoire de Mecanique – Groupe de Recherche en Genie Civil which includes characterisation, treatment of contaminants (Marot 1995), treatment by solidification/stabilisation and consolidation.

In the experiments mixes were prepared with cement (low C_3A and SO_3 contents) and with two dredged materials from Le Havre Harbour. Mix proportions were 5%, 10%, 15%, 20%, 30%, 40%, 60%, 80% and 100% by wet mass of dredged material. The results of laboratory tests indicated that many factors, such as water content, replacement level and curing time an conditions had a significant effect on the strength of the solidified material. For both materials, up to 40% replacement level, 28 day compressive strength remained below 5 to 6 Mpa. Nevertheless, from 60% replacement level, compressive strength increased rapidly in the early stages. and is overall higher than 10 Mpa. For the same dredged material the part played by the water content in strength development was brought to the fore. All solidified specimens with initial water content below 20% had compressive strengths greater than those of specimens with higher water content. However, for both materials this effect was only noticed for cement replacement levels up to 40%.

The test results for adding lime and polymer are yet to be published.

Immobilisation of organic compounds
Immobilisation of organic compounds is generally thought to be less effective than for heavy metals, however, Myers and Zappi (1989) demonstrated reductions in PCB leachability in New Bedford sediments using a solidification process. These varying results demonstrate the importance of laboratory evaluation of appropriate protocols for specific sediments, binders and contaminants prior to actual remediation work.

In-situ immobilisation
Immobilisation can be done in situ and is practiced in some countries. Chemical fixing agents are added in place. The contamination is not removed from the environment but is prevented from causing further harm. An example is the system developed by SILT NV in Belgium.

3.2.4.2 Chemical stabilisation

Fixation techniques are based on chemically fixing contaminants to prevent dispersion into the environment. There are a number of approaches. One involves adding large quantities of hydroxyl-forming substances which raise the pH of the material and cause most of the metal species to become immobile. Another technique uses a silica solution to "encapsulate" the contaminant/particle agglomerations. Research of the DPTP (1992) showed that chemical stabilisation is not always effective.

The Molecular Bonding System (MBS) is marketed by Solucorp Industries Ltd. It is appropriate for the treatment of toxic metal contaminants. It is a proprietary chemical fixation process whereby toxic metals react to form low solubility metal sulphides. It has proved to be effective for hazardous wastes in conjunction with the USEPA Superfund Innovative Technology Evaluation (SITE) (Adams and Kalb, 1998).

A trial was carried out on contaminated land in Glasgow. A former clay pit was infilled and developed as a football ground in the 1930's. The site has been contaminated with waste chromite ore and associated processing residue in the fill material. A series of trail pits were excavated and samples taken for various depths which showed Chromium level of nearly 10,000 mg/kg and a hexavalent chromium level of 760 mg/kg. The US toxicity characteristic leaching procedure (TCLP) showed chromium at 106 mg/l and hexavalent chromium at 92 mgl. Following the treatability study, a working site trial was carried out to treat approximately 100 tonnes. The soil was loaded into a hopper and fed by conveyor into a ribbon blender and MBS was added at the required rate. Water was added to catalyses the reaction and help mixing. The principle behind the process is that the chemical bonding takes place which creates metal sulphides that are stable, not pH sensitive, and resistant to leaching. The chemical reaction is immediate and the soil was discharged and stockpiled.

Samples were taken and leachability tests were carried out according to USEPA TCLP and Environment Agency test methods. They were also tested to the USEPA multiple extraction procedure (MEP), which is designated to simulate the long-term leaching effects of 1000 years of acid rain. The results of the study showed concentrations of both Chromium and Hexavalent chromium below 0.03 mg/kg.

On commercial projects a pug mill blender is used instead of the ribbon blender. The pug mill gives a capacity to treat 100 – 150 tonnes/hr. Soil is pretreated in ways described earlier to reduce particle size to less than 20mm. The oversized material and stones are then treated by crushing and/or shredding and then re-screening and sieving. The material is loaded into a hopper which feeds a conveyor and is automatically weighed. The material passes to a pug mill blending chamber where the MBS chemicals are added by computer controlled screw feeders. The chemical blend can be automatically altered by as little as 0.1% by weight. Water, if required, is added as the MBS chemical hits the soil.

The MBS process has received a mobile waste management licence from the Environment Agency, which has also been recognised by the Scottish Environment Agency.

MBS has been widely used to treat heavy metal contamination in the USA and has successfully treated arsenic, cadmium, chromium, lead, mercury and zinc. It has also been installed at the end of a process line and is treating 20,000 tonnes/year of slag from a secondary lead smelting plant, allowing the waste to be disposed to a landfill as none hazardous waste.

German experiments

Pot tests and a field trial were carried out using mud dredged from the port of Bremen (Germany) and deposited in a settling basin near Bremen. The mud is polluted with Cd and Zn. Five iron-bearing material were added to the dredged material (1% pure Fe in soil dry matter) to immobilise the heavy metals. They were:

- Red mud from the aluminium smelting industry;
- Sludge from drinking water treatment;
- Bog iron ore;
- Unused steel shot;
- Steel shot waste.

The pH and CEC were little influenced by any of these treatments, but the NH_4NO_3 and DTPA extractable amounts of Cd and Zn, and particularly the uptake of Cd and Zn by plants, were markedly reduced. It was demonstrated that red mud and precipitated Fe-bearing sludge were the most effective materials. They caused an increase in the adsorption capacity of the dredge mud with respect to Cd of about 50%. In "pot" tests, NH_4NO_3 soluble amounts of Cd and Zn in samples of soil treated with these materials were reduced by 50% (DTPA: -20%), while the uptake by plants was reduced by 25-50%. In the field trial, Cd and Zn were immobilised in the sediment to a certain extent, but less effect was observed on the concentrations in plants and soil extracts compared with the pot tests. In practice red mud is unsuitable as it contains large amounts of Cr and Al^{3+} ions. Therefore, only sludge from drinking water treatment, provided the As concentration in it is low, remains a useful material for immobilising heavy metals in polluted dredged material (Muller and Pluquet 1997).

3.2.5 Extraction technologies

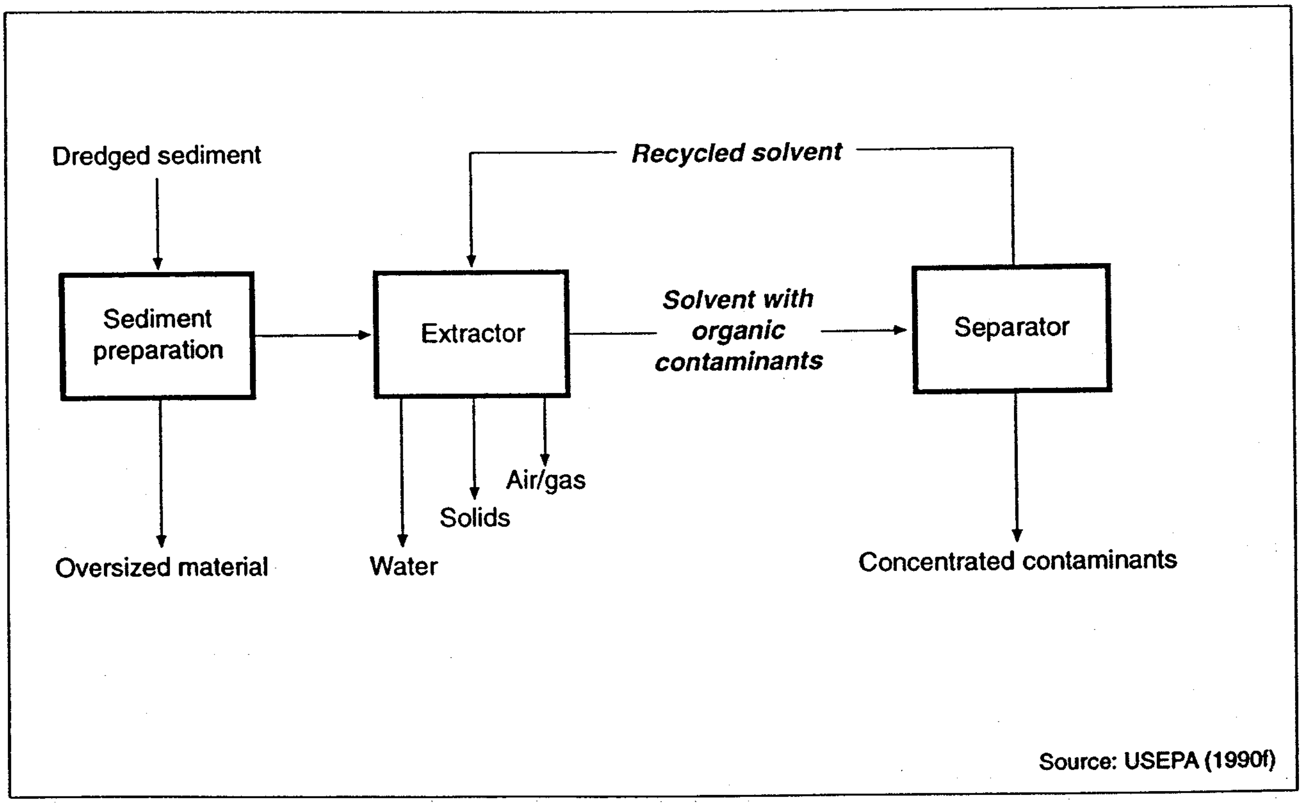
Solvent extraction processes are used to separate contaminated sediments into three fractions, particulate solids, water and concentrated organic compounds. Contaminants are dissolved or physically separated from the particulate solids using a solvent that is mixed thoroughly with the contaminated sediment. Most extraction processes do not destroy or detoxify contaminants, but they reduce the volume of contaminated material that must subsequently be treated or disposed of. Volume reductions by a factor of 20 or more are possible, depending on the initial concentration of extractable contaminants in the feed material and the efficiency of the separation of the concentrated organic (oil) stream and the water evaporated by the process. An advantage of the volume reduction is that most of the contaminants are transferred from the solid to the liquid phase, the latter being more manageable in subsequent treatment or disposal.

Solvent and surfactant extraction processes to remove oils and other organic compounds have been studied by many researchers, eg Cockrem et al (1989), Flick (undated), Dadgar and Foutch (1985) and Hall and Tiddy (1981). Both the solvent and surfactant can be recycled. Surfactant extraction can be more preferable than solvent extraction from the environmental point of view. The drawback with the surfactant extraction process is that the recovering processes are complex and hence the cost of recovering the surfactant can be high. On the other hand distillation can be a very simple and cost effective process for recovery of the proper solvent. Also, the surfactant cannot be recycled as many times as the solvent, and this reduces its applicability from the point of view of cost. Another important consideration is that most commercial surfactants are specifically designed for solubilising generic compounds, while an organic solvent can solubilise a large spectrum of organic compounds. This is particularly important in treating matrices contaminated with a wide variety of contaminants (Lakhwala and Sofer, 1991).

The primary application of solvent extraction is to remove organic contaminants such as PCB's, volatile organic compounds, halogenated solvents, and petroleum hydrocarbons. Extraction processes may also be used to extract metals and inorganic compounds but these applications involve the uses of acids and are potentially more costly. The cost of the solvent generally is a significant part of the total cost of the process so a key component is the recovery of solvents from the processed organic material and reuse them in subsequent extraction steps. Usually several extraction cycles are necessary to reduce the contamination to target levels.

Pretreatment is required to screen debris and eliminate or reduce the particle size of the material (see Section 3.1). USEPA (1988) recommends a maximum size of 5mm. The water content does not have to be reduced, in fact in some cases water must be added to enable the material to be pumped.

Extraction process can operate in batch mode or continuous mode. The basic process is shown in Fig 3.8.



Source: USEPA (1990f)

Figure 3.8 Extraction process

Sediment and solvents are mixed together in an extractor. Extracted organic compounds are removed using the solvent and are transferred to a separator where the solvent and organic compounds are separated from the water and the contaminants are separated from the solvent by changes in temperature or pressure, or differences in density. Concentrated organic contaminants are usually associated with an oil phase, which is removed from the separation chamber for post treatment. The solvent is recycled to the extractor to remove additional contaminants. The cycle is repeated several times before the solids are finally removed from the extractor.

When the solids are removed they contain a certain amount of the solvent. The solvents selected generally vaporise or are biodegradable. Some processes incorporate a further stage to remove the solvents by distillation.

Experiments have been carried out in the Netherlands under the DPTP programme (DPTP 1992), cleaning sediments contaminated with organic micropollutants such as fluorene, phenantrene, chrysene and benzo(a)pyrene (Van Dillen, 1991). Solvent extraction was carried out with toluene and triethylene. Toluene was selected because it is effective in dissolving PAH's. Triethylene has the very useful property of forming one phase with water under 15°C. At higher temperatures water and amine can be separated.

A number of proprietary processes are commercially available. They have been tested in the US and two have been used in demonstration projects. A brief description of these processes is given in the following sections.

3.2.5.1 Basic Extractive Sludge Treatment Process (BEST^R)

The BEST process (Resources Conservation Co) uses a combination of tertiary amines, usually triethylamine (TEA) as a solvent. The first extraction is conducted at temperatures below 4^{0}C where TEA is soluble with water, and at a pH greater than 10. Hydrocarbons and water in the sediment simultaneously dissolve with the TEA, creating a homogenous mixture (USEPA, 1992). In the next step solids are separated from the liquid mixture by settling. The remaining solvent is removed from the solids fraction by indirect steam heating. Water is separated from the TEA-organic compound mixture by heating the solution to temperatures above the miscibility point (about 54^{0}C). Organic compounds and TEA are separated by distillation and the TEA is recycled to the extraction step. This process was demonstrated at the Grand Calumet River (USACE Chicago, 1994). Bench scale tests were performed for Buffalo River, Saginaw River and Grand Calumet River sediments (cited in USEPA, 1994).

3.2.5.2 CF Systems Solvent Extraction

The solvent extraction process offered by CF Systems uses compressed propane at supercritical conditions as the solvent. Sediment is screened to remove oversized material and debris and is then pumped through the system as a slurry in a continuous mode. The solvent is mixed with the sediment under normal temperatures and high pressures. Organic compounds are extracted from the sediment and water into the solvent. The solvent-organic compound stream is removed from the extractor and the propane is separated from the organic compounds by reducing the pressure and allowing the propane gas to vaporise. After recompression the gas is recycled to the extraction stage. Three or more cycles are usually necessary to achieve at reduction factor of 90-98% (USEPA 1992). This process was demonstrated using sediments from the New Bedford River site (USEPA, 1990a,b).

3.2.5.3 Carver-Greenfield Process

The Carver-Greenfield process (Dehydro-Tech Corp.) is a physical process that can be used to separate oil-soluble organic compounds from contaminated sediments. Pretreatment is similar to other extraction processes and, again, dewatering is not necessary. The process involves dissolving the contaminants in a food-grade oil with a boiling point of about 204^{0}C. 5-10kg of carrier oil are added to each 1kg of solids in a mixing tank. Three or more cycles may be necessary. The slurry is transferred from the mixing tank to a high-efficiency evaporator where the water is removed. The oil is separated from the dewatered solids initially by centrifugation and then by a hydro-extraction process that uses hot nitrogen gas to strip the remaining oil from the solids. After separating the contaminants from the oil by distillation the oil is recycled to the extraction stage and the concentrated contaminants are further treated or disposed of.

Drilling-mud waste has been treated in this way but there is no record of it being used for sediments although it would seem to be applicable.

3.2.5.4 Soil Washing

The term soil washing is generally used to describe extraction processes that use a water based fluid as the washing medium (USEPA, 1990c). Many soil washing processes rely on particle size separation to reduce the volume of contaminated material. These were discussed in Section 3.1. Other water-based techniques involve dissolving or suspending the contaminants in the water-based fluid. Because most sediment contaminants are tightly bound to particulate matter, water alone is not a suitable extraction fluid. Surfactants, acids or chelating agents may be used with water to effect separation. The particle size and type of contaminant are important factors. Sediment containing mainly silt and clay is only marginally suitable for this type of treatment.

Cleaning of contaminated sediments by washing processes using water as extraction medium is economical if the concentrations of silt are lower than 25%. Conventional mechanical physical washing processes deliver a cleaned sand fraction and a contaminated silt fraction. Due to the lack of economical treatment processes for the contaminated silt fraction this part of the sediment has to be brought to special waste disposal sites after de-watering. A new technique is under development, that enables greater separation of organic and mineral particles thus increasing the amount of material recyclable and reducing the amount for disposal or more expensive treatment. The process is patented as the ASRA^R-DEMI Process (Luther et al, 1997).

The main characteristics of the new process are:
- A pump system which treats the suspension by high energy impact under partly cavitating conditions;
- A special spraying process in the following separation step.

The sediment is filled into a special container which serves as a feeding and pre-processing system. The pre-treated suspension leaves this feeding container and is pumped to the mobile ASRA plant. The mobile ASRA plant separates conventionally the sediment suspension by sieves, hydrocyclones and an upstream classifier into the coarse fraction, sand fraction and silt fraction.

It is important for the DEMI process that the suspension has been pre-treated by cavitation. The fluid containing both organic and mineral particles is transported through two hydrocyclone systems within ASRA plant toe the DEMI process. Organic particles and organic layers on the particles have been treated by the impact energy generated by pumps. The main activator of the DEMI plant is a rotating disc on which the suspension is sprayed, the aerosols settle slowly to the bottom of the tank. Due to the fact that the bed within the tank has a small slope the air saturated suspension is transported with the water film to the centre of the tank. The mineral fraction settles directly and remain as a silt bed within the tank, while the organic part and a small amount of lost mineral particles can be gathered together with the process water at the outlet.

A conventional flotation/flocculation facility can be integrated. This water treatment plant produces process water recycled to the ASRA-DEMI plants, cleaned overflow water and sludge with approximately 50% water content.

The US Bureau of Mines evaluated acid extraction for heavy metals in Great Lakes sediments from three sites and found minor reductions in sediment metal concentrations (Allen, 1995). The use of surfactants may be successful in removing organic compounds from sandy sediments.

3.2.5.5 EDTA extraction

EDTA (ethylene diamine tetra acetic acid) is a complexing agent that solves heavy metals. In early experiments removal efficiencies of between 60 to 90% were demonstrated for cadmium, zinc, lead and copper. The advantage of using a complexing agent instead of acid is the possibility of recycling and reusing it in the process. Laboratory tests were scaled up to a pilot project using contaminated soil but the experiment failed. The following reasons for failure were given (Rienks 1997):

- The treatment results depend strongly on the speciation of heavy metals, that is to say the type of metal compound present and their mechanisms of binding to soil particles;
- The experience with separation and recycling from the extractant after treatment of fines is insufficient;
- The influence of common soil constituents like iron, aluminium, manganese and magnesium on the consumption of EDTA is no well known but is essential for the efficiency of the extraction.

3.2.5.6 Acetone extraction of PAHs

In Dutch experiments acetone was chosen as the solvent for a number of reasons:
- Organic solvents solve organic pollutants
- Completely mixable with water;
- Low toxicity;
- High extraction efficiencies
- Cheap and generally available;
- Good prospects for recycling.

In the experiments extraction efficiencies of more than 98% were achieved for PAH. An acetone water mixture of 80%m/m acetone gives the best results. A liquid/solid ration of 15l/kg ds was applied. Extraction experiments were simulated by counter current flow and cross flow. A plural step extraction by counter current flow is to be preferred for scaling up the process because of extraction efficiencies and a tendency of channeling at the cross flow percolation experiments.

Based on the results a design of a mobile treatment plant with a capacity of 10 tonnes dry solids per hour was made for treatment of separated fines from sediments. All parts are existing technology except for the extractor. This is the main gap in knowledge that has to be filled before scaling up the process. The extraction takes place in a settler, combined with a lamellae separator. In the settler, a sediment/acetone/water slurry is led downwards while a 80% water/acetone mixture is pumped in counter current upwards. This extraction procedure was tested in the laboratory in a column with a diameter of 0.05m The tests revealed mixing problems in the horizontal section of the settler, probably induced by differences in density between the slurry and the extraction agent. Alternatives like a number of hydrocyclones (0.01 m diameter) should be used for treating fines, which means a high pressure loss and subsequent high energy consumption as well as the risk of accumulation of fine particles in the process. There are plans to test a new settler mixer (Rienks 1997).

According to Rulkens et al (1997) the use of acetone is particularly attractive when the sediment consists mainly of clayey particles polluted with contaminants which are not or are not easily biodegradable. Rulkens reports the tests carried out at laboratory scale on sediments from the Amsterdam Petroleum Harbour. This sediment is characterised by a high proportion being <0.063mm, a high percentage of organic matter (12%), a high concentration of PAH (500 – 2000 mg/kg total EPA-PAH) and high concentration of mineral oil (6000 – 10000 mg/kg). The process consisted of a counter-current flow extractor, a separator for the sediment, a post treatment step to remove residual acetone, a distillation column to recover the acetone for re-use and to concentrate the pollutants, and a polishing step for the water to be discharged. The treatment costs by this method were estimated at 115 NGL/tonne dry matter.

A schematic diagram illustrating the process is given in Fig 3.9.

3.2.5.7 Extraction with supercritical carbon dioxide

This process is operated at elevated temperature and pressure. At supercritical conditions, compounds show physical properties of both liquid and gas. The density of the supercritical medium is comparable to that for liquids, whereas the viscosity and diffusivity are comparable to those for gases. The supercritical temperature of carbon dioxide is 31^0C; the supercritical pressure is 74 bar. Supercritical carbon dioxide behaves like an apolar organic compound. For optimum extraction of slightly polar compounds like PAH, it is necessary to add an entrainer. An entrainer is an organic solvent with enlarges the solubility of eg PAH in the supercritical CO_2 and also increases the desorption of eg PAH from the sediment particles (Rienks 1997).

In laboratory experiments acetone, dichloromethane and toluene were used as entrainers. Toluene gave the best results. The samples were taken from the fine fraction of a sediment heavily contaminated with mineral oil and PAH. Optimum extraction results were found for dried fines: 85-90% removal of mineral oil and 70-80% for PAH sum. PAH with 4 or 5 aromatic rings were extracted for 40% at most whilst PAH with 2 or 3 rings were extracted for 99%. A similar phenomenon was found for mineral oil compounds: heavy compounds (C32 – C40_ were extracted for 60% at most. Undried fines with higher water content could not be extracted with good results. With the amount of drying necessary as pre-treatment, thermal desorption is considered to be a more obvious alternative.

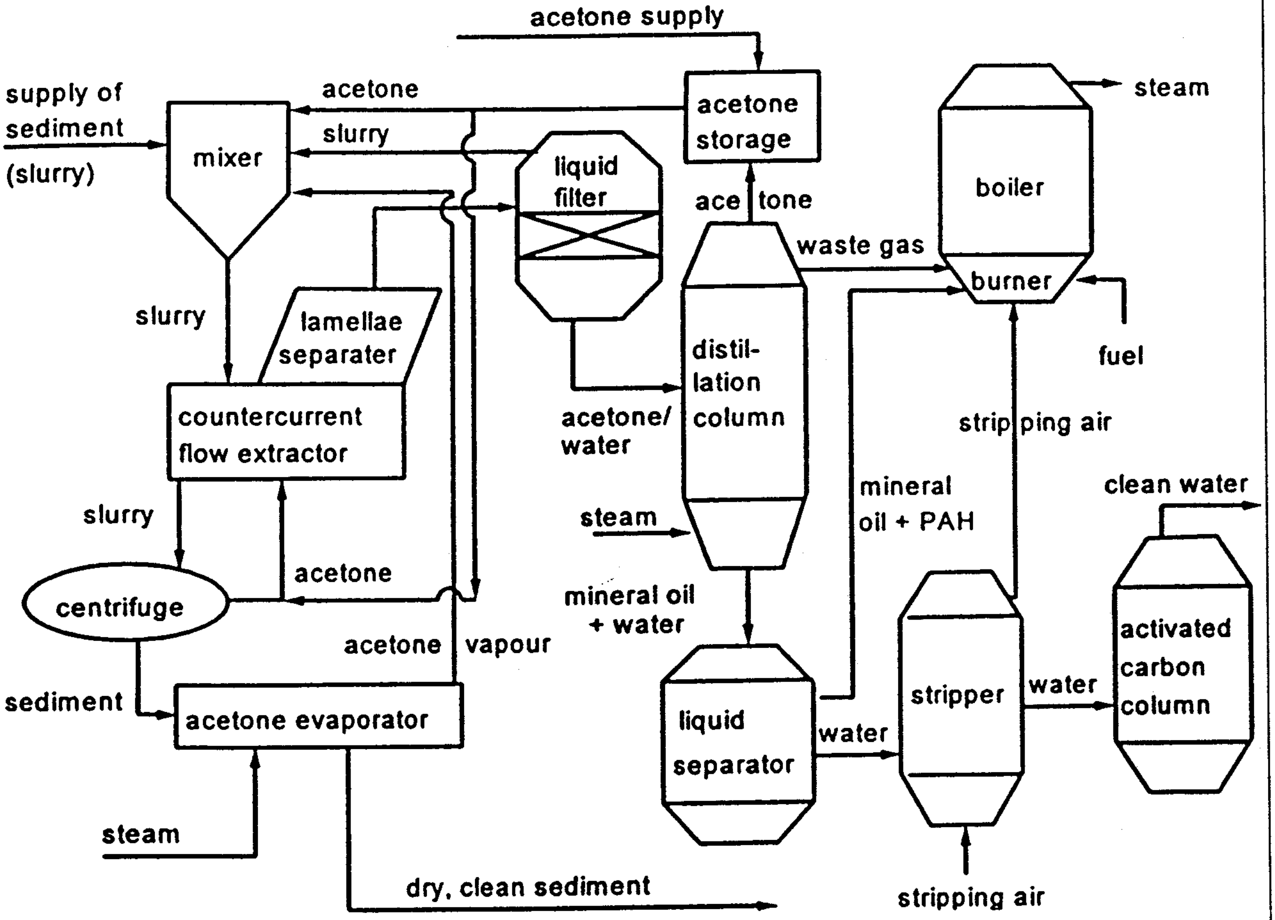


Figure 3.9 Acetone extraction system (Rulkens 1997)

3.2.5.8 Other extraction processes

Other extraction processes are emerging that have the potential for removing organic and perhaps inorganic compounds from contaminated sediments. A list, compiled from the SEDTEC database (Wastewater Technology Centre, 1993) and reproduced in USEPA (1994) is given in Appendix 2. This lists the name of the process, the class of contaminant treated and the extraction fluid or other medium used to separate the contaminants. Most vendors do not state the particular solvent used, stating that it depends on the contaminant concerned.

Table 3.9 Factors affecting solvent extraction processes

Factor	Effect
Particle size	It is more difficult to extract contaminants from fine grained material. Larger particles may not pass through close clearances in process equipment and may interfere with the pumping of sediment slurry (where required). Acceptable particle size depends on the process and the scale of the plant. Ranges of 5 – 25mm have been reported as maximum values.
Solids content	Depends on the process selected. Most require slurries of 20-60% solids. Some batch processes may require minimal water, depending on the solvent used.
Solvent characteristics	Most organic solvents are relatively volatile, requiring control of emissions. Some solvents may be toxic to some organisms, requiring very efficient separation of the solvent from the solids prior to disposal.
pH	Depends on the process selected. For example, pH adjustment to >10 is required for triethylamine extraction.
Presence of detergents and/or emulsifiers	Adversely affects oil/water separation. Retains contaminants in competition with solvents. Foaming hinders separation and settling.
Metals	Metals in fine-grained sediment are not easily removed by solvent extraction processes. Organically bound metals may be extracted and become a component of an organic waste stream, creating additional restrictions on disposal.
Types of organic compound	Solvent extraction is less effective for high molecular weight organic compounds and very hydrophobic substances because of a strong affinity for fine-grained particles.
Reactivity	Certain contaminants are incompatible with some solvents and may react adversely. Requires careful selection of contaminants and laboratory testing.

3.2.6 Chemical treatment technologies

Chemical treatment is defined here as the process in which chemical reagents are added to a sediment matrix for the purpose of destroying contaminants (as opposed to extracting them, described in the previous section). Certain immobilisation, extraction and thermal procedures also involve chemical inputs, but they are typically to alter the phases of the contaminant to facilitate its removal or binding. A clear distinction cannot always be made and some overlap exists between this and other sections of the report.

Chemicals are typically added to contaminated sediment in batch operations in a process vessel. Chemical treatment may destroy contaminants completely, may alter the form of the contaminants so they are amenable to other treatments or may be used to optimise process conditions for other treatment processes. Treated sediments may then be permanently disposed of or put to some beneficial use, depending on the nature and extent of residuals, including reagents and contaminants.

Averett et al (1990) reviewed eight general categories for their suitability for use with dredged material. Of these chelation, dechlorination and oxidation of organic compounds were considered the most promising. These are described below. Some other promising technologies are also discussed.

3.2.6.1 Chelation Processes

Chelation is the process of stable complex formation (a chelate) between a metal cation and a ligand (chelating agent). This process could also be called an Immobilisation process. Some extraction processes also use chelating agents. Binding of the metal cation in a stable complex renders it unavailable for further reaction with other reagents in chemical or biological systems. The stability of a complex generally increases as the number of bonds increases between the ligand and metal cation (Snoeyink and Jenkins, 1980). A ligand forming a single bond is known as monodentate; a ligand forming two bonds is bidentate and a ligand forming more than two bonds is known as polydentate. Ethylenediaminetetracetic acid (EDTA) is a well known example of a polydentate ligand (Brady and Humitson, 1986). pH is one of the most important parameters that affects the treatment process. Efficiency varies with the chelating agent and dosage used.

The ENSOL and LANDTREAT process uses a polysilicate as an adsorptive agent called LANDTREAT, to solidify metal hydroxide silicate and a proprietary chelating agent. The process is carried out in an enclosed, continuous-reaction chamber (Wastewater Technology Centre 1993). The process is available at the full scale commercial level.

3.2.6.2 Dechlorination Processes

Dechlorination processes remove chlorine molecules from contaminants such as PCB's, dioxins and pentachlorophenol through the addition of a chemical reagent under alkaline conditions at increased temperatures (USEPA 1990d,e). The resulting products are much less toxic than the original contaminants. Typically, chemical reagents are mixed with the contaminated sediments and heated to temperatures of 110-340^{0}C for several hours, producing the chemical reaction and releasing steam and volatile organic vapours. The vapours are removed from the processor, condensed and further treated using activated carbon. The treated residue is rinsed to remove reactor by-products and reagent and is then dewatered prior to disposal. Adjustment of the pH of the residue may also be required. The wastewater produced may require further treatment. Processing feed streams with lower solids contents, such as sediments, require greater amounts of reagent, increase energy requirements and produce larger volumes of wastewater for disposal, all distinct disadvantages of this process. Some proprietary systems are described below.

APEG Chemical Dehalogenation Treatment

This process typically uses an APEG to treat aromatic halogenated compounds (USEPA, 1990d). Potassium hydroxide (KOH) is most commonly used with polyethylene glycol (PEG), to form the polymeric alkoxide potassium polyethyleneglycol (KPEG), although sodium hydroxide has also been used and is less expensive. Another reagent is KOH or sodium hydroxide/tetraethylene glycol, which is more effective on halogenated aliphatic compounds. Dimethyl sulfoxide (DMSO) may be added to enhance rate kinetics (USEPA, 1992). Products of the reaction are a glycol ether and/or a hydroxylated compound and an alkali metal salt, water soluble by-products.

DeChlor/KGME Process

KGME is a proprietary reagent of Chemical Waste Management Inc, and is the active species in a nucleophilic substitution (dechlorination) reaction. Principally KGME is used for liquid phase halogenated compounds, particularly PCB's. It has been successfully used to treat sediments at laboratory scale (USEPA 1992).

Base-Catylysed Dechlorination Process

The base-catylysed dechlorination process combines chemical addition with thermal inputs to dechlorinate organic compounds without the use of PEG (USEPA, 1992). The mechanism appears to be a hydrogenation reaction (Rogers, 1993). The hydrogen source is a high-boiling-point oil plus a catalyst. The process has been used for both liquids and solids in "in situ" and "ex-situ" applications.

Ultrasonically Assisted Detoxification of Hazardous Material

This process effects the chemical destruction of PCB's in soil using an aprotic solvent, other reagents and ultrasonic irradiation (USEPA, 1992). The dechlorination of PCB's in the process is believed to result from a nucleophilic substitution reaction, although this is not verified. The purpose of the ultrasonic irradiation is to add heat to the reaction. The technology is currently being tested using a moderate-temperature, heater reactor and reflux column (Kaszalka 1993). The process is suitable for ex-situ application only. To be economically feasible the reagents must be recovered. The technology currently exists at pilot scale development level only.

3.2.6.3 Oxidation processes

Chemical oxidation involves the use of chemical additives to transform, degrade or immobilise organic wastes. Oxidising agents most commonly used (singly or in combination with ultraviolet light) are ozone, hydrogen peroxide, peroxone (combination of ozone and hydrogen peroxide), potassium permanganate, calcium nitrate and oxygen. The use of ozone, peroxide and peroxone has come to be known as advanced oxidation processes. Strictly defined, oxidation is the addition of oxygen to a compound (creation of carbon to oxygen bonds) or the loss of electrons from a compound (increase in positive valence). Oxidation is used to transform or break down compounds into less toxic, mobile or biologically available forms. Theoretically, compounds can be decomposed completely to carbon dioxide and water. Adequate process control of pH, temperature and contact time is important to prevent the formation of hazardous intermediate compounds such as trihalomethanes, epoxides and nitrosamines, from incomplete oxidation.

Oxidation is commonly used to treat amines, phenols, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans and certain pesticides in liquid waste streams (USEPA 1991b). It can also be used on soil slurries and sludge. The effectiveness of oxidation depends on the organic compound as shown in Table 3.10.

Table 3.10 Suitability of organic compounds for oxidation

Oxidation suitability	Compounds
High	Phenols, aldehydes, amines, some sulphur compounds
Medium	Alcohols, ketones, organic acids, esters, alkyl-substituted aromatics, nitro-substituted aromatic compounds, carbohydrates
Low	Halogenated hydrocarbons, saturated aliphatic compounds, benzene

Oxidation is non-selective and all chemically oxidisable material (including detritus and naturally occurring organic matter) will compete for the oxidising agent. It is not applicable to highly halogenated organic compounds. Certain contaminants such as PCB's and dioxins. That will not with ozone alone, require the use of UV light with the oxidising agent.

The LANDTREAT and PETROXY process uses a synthetic polysilicate (LANDTREAT) for adsorption of organic compounds to facilitate the oxidation by the PETROXY reagent, which includes a combination of hydrogen peroxide and other additives. A secondary reaction is the conversion of heavy metal cations to metal silicates on active sites of the LANDTREAT (Wastewater Technology Centre, 1993).

3.2.6.4 Other chemical treatment processes

<u>Chemical and Biological Treatment Process</u>

This combines chemical and biological treatment for the purpose of enhancing biodegradation (USEPA 1992). The mechanism provides oxygen for biological uses, oxidation of organopollutants and alteration of the soil matrix. The process produces chemical intermediates that are both more bio-degradable and, due to apparent alteration of the soil matrix, more bio-available. This can be beneficial with high waste concentration that would typically be toxic to micro-organisms.

D-Plus (Sinre/DRAT)

This process involves the use of chemical imputs to stimulate enzymes and to provide a favourable chemical environment (alkaline, reducing, anaerobic) for hydrogenation, dehalogenation, and hydrolysis. A bio-chemical process, the technology uses heat to break carbon-halogen bonds and to volatilise light organic compounds. There is potential to develop this technology for in-situ applications.

Table 3.11 Summary of chemical treatment technologies (after USEPA 1994)

Technology	Application	Specifications and limitations	Efficiency
Chelation Processes			
ENSOL AND LANDTREAT	Ex situ treatment of metals in soils and dewatered sediments	Full scale commercial, portable. Feed rate $90m^3$ in 8 hours. Chemically inert, multibound metal silicate complex formed.	>99% reduction in metals solubility
Dechlorination processes			
APEG Chemical Dehalogenation	Ex situ soils, sludges, sediments and oils containing: • PCB's • Dioxins • Furans • Some halogenated pesticides May not be suitable if contaminants other than halogenated compounds are present. Potential effectiveness for halogenated volatile organic compounds and halogenated semivolatile organic compounds in sediments, oils, soil, sludge and halogenated pesticides in sediments and sludge	Requires dewatering of sediments to no less than 93%. Requires nitrogen atmosphere. Reactions occur at 120 – 180^0C unless <93% solids. By-products include: • Chloride salts • Polymers • Heavy metals Post-treatment soil washing may be required to remove residual reagent and by-products.	PCB concentrations up to 45000ppm have been reduced to <2ppm per congener. Dioxins and furans have been reduced to non-detectable levels (1ppt detectable level)
KPEG Process	Waste oils containing dioxins Diesel fuel containing PCB's, dioxins and chlorobenzenes. Soil containing PCB's	Same as APEG	99.999% reduction of PCB's in field study (Chan et al, 1989)
Dechlor/KGME	Liquid phase halogenated compounds, particularly PCB's. Dechlorination of liquid and solid wastes to allow for a proper disposal (dioxins) Most effective on highly chlorinated PCB's (Palmer, 1993) Numerous bench scale demonstrations on PCB's, dioxins and furans.	PCB's treated in both liquid and solid matrices. Residuals may require post-treatment such as incineration. Reaction time is 3-6 hours at 100^0C. Nitrogen atmosphere required in reactor headspace.	Up to 99.99% removal of PCB's in liquid and solid matrices.
Base-Catalysed Dechlorination	In situ or ex-situ treatment of solid or liquid waste streams contaminated with: • Halogenated volatile organic compounds • Halogenated semi-volatile organic compounds • PCB's • PCP • Halogenated herbicides • Halogenated pesticides • Dioxins	High clay and low solids content may increase treatment costs slightly. Ex-situ feed material rate: approx. 1tonne/hr batch. Residuals: • Clean solids • Clean solids in oil • Clean gas • Treated water.	>99.99%reduction of PCB's Treatment to <10ppb PCB (Rogers et al 1993)

	• Furans		
Ultrasonically Assisted Detoxification (dehalogenation)	Ex-situ treatment of soil contaminated with chlorinated hydrocarbons including: • Pesticides • Herbicides • PCP • Dioxins • Furans Currently at pilot scale development.	Solvent recovery is key to lowering costs.	>99% destruction of PCB's at 25 – 1700ppm.
D-PLUS (Sinre/DRAT)	Contaminated sediments containing: • Volatile organic compounds • Semivolatile organic compounds	Pilot scale development stage: could easily treat up to 900tonnes/batch with existing equipment but may not be economic without further scale-up.	90-99% reduction of PCB's at initial concentrations of 3000ppm
Oxidation Processes			
LANDTREAT and PETROXY	Ex-situ treatment of: • Halogenated organic compounds • Hydrocarbons • Volatile organic compounds In soils and dewatered sediments.	Feed rate 90m^3/hr in METS machine. Emissions: • CO_2 • H_2O • Basic calcium carbonate/bicarbonate • Carbon filtered air • <10ppm volatile organic compounds	Not given

3.2.7 Bioremediation technologies

Bioremediation, sometimes called biorestoration, is a managed or spontaneous process in which microbiological processes are used to degrade or transform contaminants to less toxic or non-toxic forms. Microorganisms depend on nutrients and carbon to provide the energy needed for their growth and survival. Degradation of natural substances in soils and sediments provides the necessary food for the development of microbial populations in these media. Bioremediation technologies harness these natural processes by promoting the enzymatic production and microbial growth necessary to convert the target contaminants to non-toxic end products.

Biological treatment has been used for decades to treat domestic and industrial wastewater. In recent years it has been demonstrated as a technology for destroying some organic compounds in soils, sediments and sludges. The chemical and physical structure of organic compounds affects the ability of microorganisms to use them as a food source. The degradation potential for different classes of organic compounds is illustrated in Fig 3.10. They show particularly good prospects for dredged material contaminated with petroleum hydrocarbons and PAH's (PIANC 1996, Stockman and Bruggeman 1993 and Wardlaw, 1994).

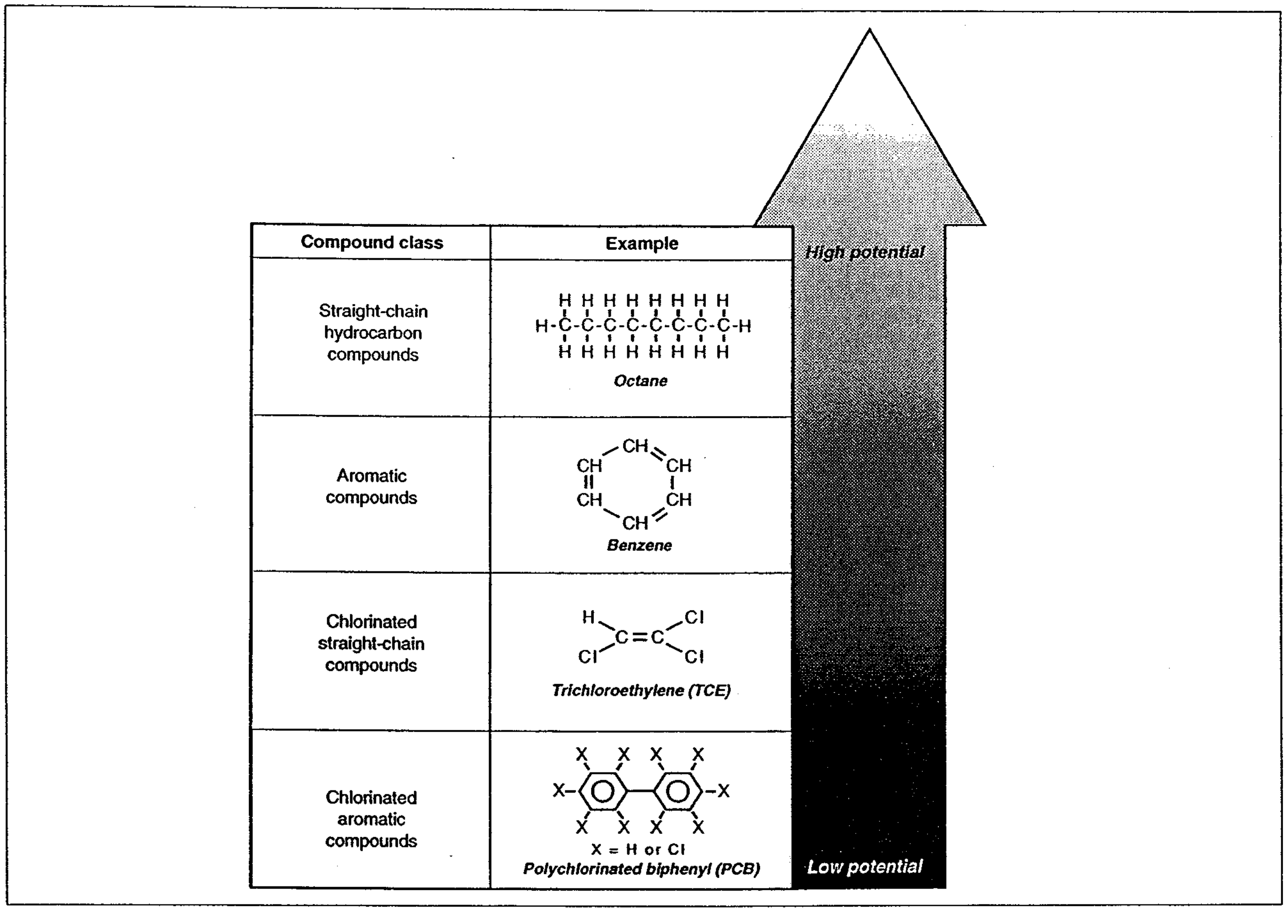


Figure 3.10 **Biodegradation potential for classes of organic compounds**

Bioremediation of organic compounds in sediment is a complex process, and its application to specific compounds is based on an understanding of the microbiology, biochemistry, genetics, metabolic processes, structure and function of natural microbial communities. Microbiology must be combined with engineering to develop effective bioremediation processes. A workshop held in 1991 provides a discussion of the technologies with an emphasis on the microbial and chemical processes involved (Jafvert and Rogers, 1991).

The efficiency of biological treatment seems to be highly dependent on the form in which the pollutants are adsorbed to the sediment. An advantage of biological methods is that the contaminated dredged material stays intact. A great deal of research is being directed to this area, and breakthroughs in treatment efficiency are occurring rapidly (DPTP 1992).

Many of the more persistent contaminates in the environment, such as PCB's and PAH's are resistant to microbial degradation because of:

- The compound's toxicity to the organisms;
- Preferential feeding of microorganisms on other substrate;
- The microorganism's lack of genetic capability to use the compound as a source of carbon and energy;
- Unfavourable environmental conditions in the sediment for propagating the appropriate strain of microorganisms.

Alteration of the environmental conditions can often stimulate development of appropriate microbial populations that can degrade the organic compounds. Such changes may include adjusting the concentration of the compound, pH, oxygen concentration, or temperature, or adding nutrients or microbes that have been acclimatised to the compound.

A summary of the sediment characteristics and environmental conditions that limit bioremediation processes and actions to mitigate those effects is given in Table 3.12.

Table 3.12 Characteristics that limit biodegradation processes (after USEPA, 1994)

Limiting characteristic	Reason for effect	Mitigation action
Variable sediment composition	Inconsistent biodegradation caused by variation in biological activity	Dilution of contaminated sediment, eg increased mixing or blending of sediment
Non-uniform particle size	Reduces the contact with micro-organisms.	Physical separation to remove coarse-grained material, particularly for bioslurry
Water solubility	Contaminants with low solubility are harder to biodegrade	Addition of surfactants
Biodegradability	Low rate of destruction inhibits the process	Addition of microbial culture capable of degrading particularly difficult compounds. Longer residence time.
Temperature outside 15-35^{0}C range	Less microbial activity outside this range	Temperature monitoring and adjustment.
Nutrient deficiency	Lack of adequate nutrients for biological activity.	Adjustment of the carbon/nitrogen/phosphorus ratio
Oxygen deficiency	Lack of oxygen limits the rate	Oxygen monitoring and adjustment
Insufficient mixing	Inadequate microbe – solids – organic contact.	Optimise mixing process. Increase permeability.
pH outside 4.5 – 8.8 range	Inhibition of biological activity	Sediment pH monitoring. Addition of acidic or alkaline compounds to adjust.
Microbial population	Insufficient population results in low rates	Addition of culture strains
Water and air emissions	Potential environmental and/or health effects	Post treatment emission collection and treatment processes (eg air scrubbing, carbon filtration)
Presence of elevated, dissolved concentrations of: • Heavy metals • Highly chlorinated organic compounds • Some pesticides and herbicides • Inorganic salts	Can be highly toxic to micro-organisms.	Pretreatment processes or dilution with amendments to reduce the concentration of toxic compounds in the constituents in the sediment to the non-toxic range.

Biodegradation of refractory organic compounds is not uncommon in nature but can take many years. The key to improving the usefulness for cleaning up contaminated sites is to determine how to accelerate the process for the target contaminants.

Ideally it would be carried out in situ but there are some problems:

- The complexity of the sediment water ecosystem;
- The difficulties in controlling physical and chemical as well as biological processes in the sediment;
- The need to adjust environmental conditions for various stages of degradation.

Considerable research is underway on overcoming the in-situ problems, however, the best prospects for treating contaminants at present are engineered treatment systems in which environmental conditions can be carefully controlled and adjusted as the bio-transformation processes progress with time.

Biodegradation is accomplished either aerobically or anaerobically. Aerobic respiration is energy yielding microbial metabolism in which the terminal electron acceptor for substrate oxidation is molecular oxygen. Carbon dioxide and water are the end products. Free oxygen must be present for aerobic reactions to occur. Anaerobic respiration is energy-yielding metabolism in which the terminal electron acceptor is a compound other than molecular oxygen, such as sulphate, nitrate or carbon dioxide. Methane, sulphides and organic acids are the end products. Aerobic processes are generally more rapid and provide a more complete degradation of the organic compounds than anaerobic processes. However, some compounds can only be changed by anaerobic organisms, for example, dechlorination of the more highly chlorinated PCB's. On the other hand, the less chlorinated PCB's are susceptible to degradation by aerobic organisms. Sequential anaerobic treatment followed by aerobic processes appears to offer an effective destruction technology for PCB's (Quensen et al, 1991).

Heavy metals may be removed by plant cultivation technology and biotechnological leaching, the latter using the fact that many bacterial activities produce lactic acid which can dissolve metals.

The following sections address a number of specific processes. Pretreatment for most of these include the removal of oversized particles and possible adjustment of water/solids ratio.

3.2.7.1 Bioslurry processes

Bioslurry reactors are a relatively new technology that has been applied to contaminated sediments mostly in the last 10-15 years. There have been a number of pilot scale applications in the US and few full-scale installations. Bioslurry reactors are best suited to treating fine-grained materials that are easily maintained in suspension. A sediment-water slurry is continuously mixed with appropriate nutrients under controlled conditions in an open or closed impoundment or tank. Aerobic treatment, which involves adding air or another oxygen source, is the most common mode of operation. However, conditions suitable for anaerobic micro-organisms can also be maintained in the reactor where this oxic state is an essential step in the biodegradation process. Sequential anaerobic/aerobic treatments are also possible in these systems. Contaminants with potential for volatilisation during the mixing and/or aeration process can be controlled using emission control equipment. A schematic diagram of an aerobic bioslurry process is shown in Fig 3.11 below. Systems for treating soils or sediments are often operated in batch mode because typical retention times are 2 –12 weeks. Once the treatment period is complete the solids may be separated from the water and disposed of separately. The slurry solids concentrations range from 15 – 40%. Adjustment in solids contents for this treatment process may be minor.

The degradation of PCB's using the bioslurry reactor technology was investigated by General Electric Company (Abramowicz et al 1992). Researchers concluded that between 35 – 55% of the initial PCB's were degraded over a 10 week test period in reactors amended with biphenyl. Remediation of contaminated sediments from Toronto Harbour, Ontario, was tested in pilot scale reactors in 1992 (Toronto Harbour Commission, 1993). Although complicated by analytical interferences, the results showed that oil and grease was completely degraded in several weeks, with a partial degradation of PAH's.

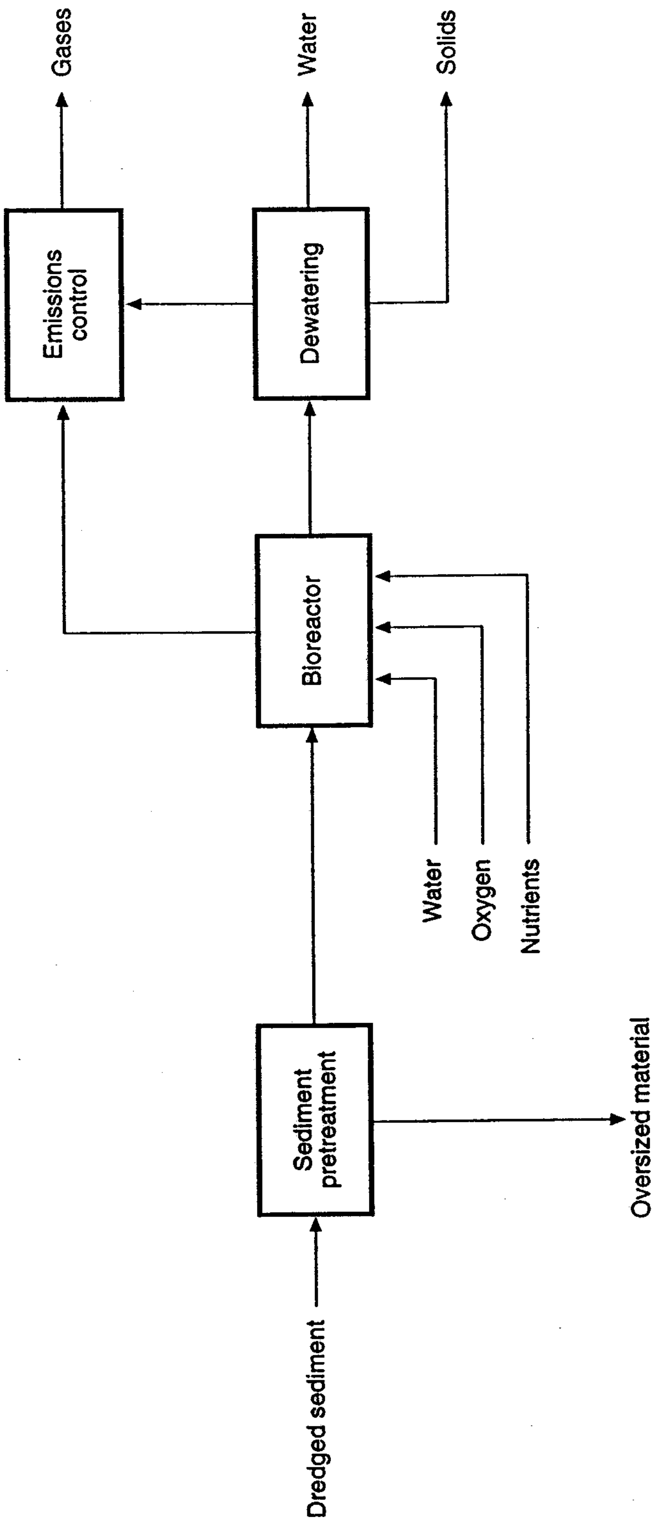


Figure 3.11 Aerobic bioslurry process (after USEPA, 1994)

3.2.7.2 Contained Land Treatment and Landfarming Systems

Contained land treatment

Contained land treatment systems have been demonstrated in Europe. They require mixing of the sediment followed by placement in an enclosure such as a building or tank on a pad or prepared surface. The enclosure protects the material from precipitation, moderates temperature changes, allows moisture control and provides the capability to control volatile organic compound emissions. A schematic diagram is shown in Fig 3.12.

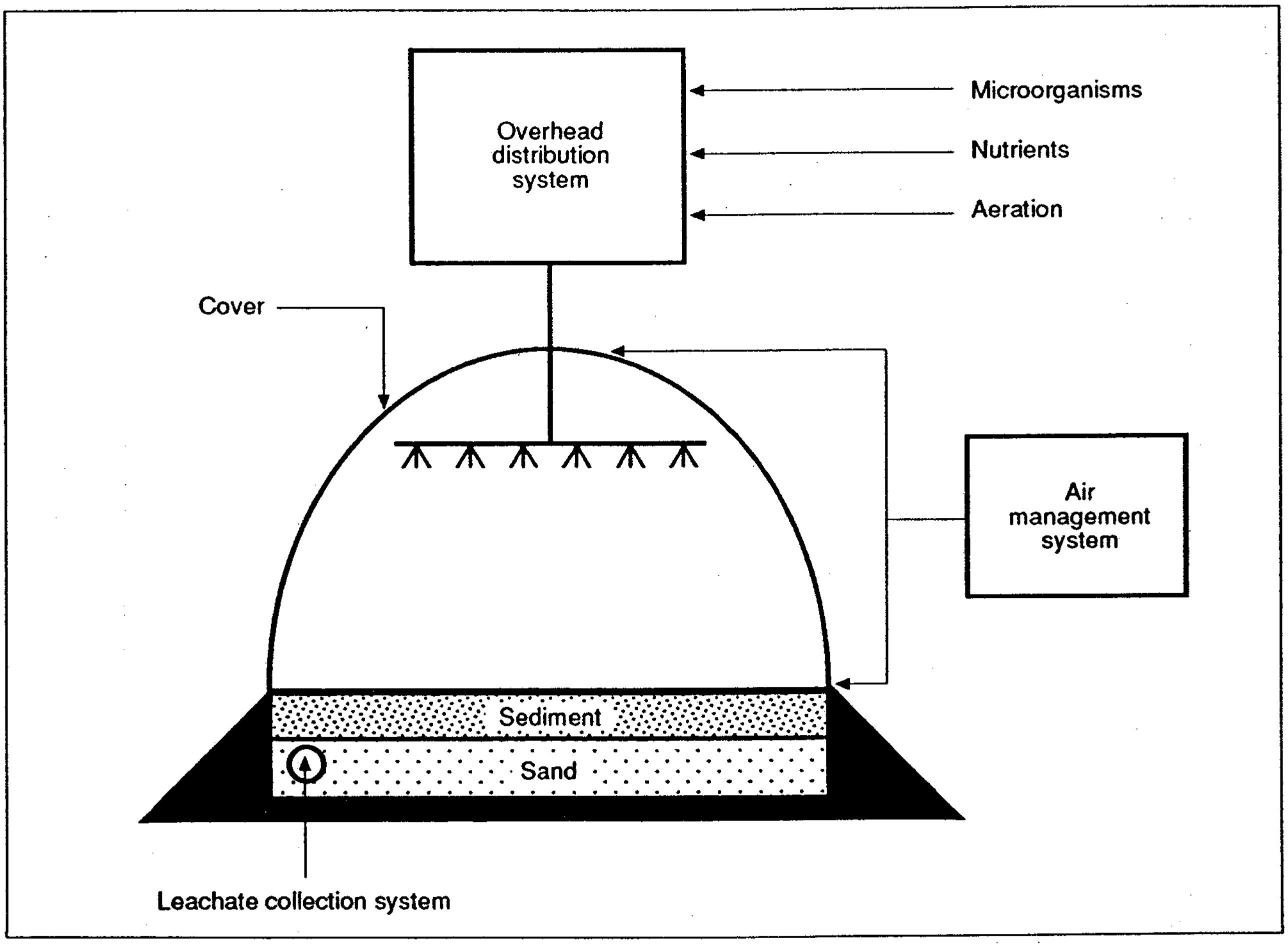


Figure 3.12 Contained land treatment system (after USEPA, 1994)

Leachate from the sediment is collected by underdrains for further treatment as necessary. The layer of sediment treated for each lift is generally no deeper than 150-200mm. Regular cultivation of the sediments and the addition of nutrients, and, in some cases, bacterial inocula, are typically required to optimise the environmental conditions for rapid bioremediation. The excess water associated with the sediment as it is placed in the treatment bed may create operational problems for start-up and will probably require that the system be designed for lateral confinement of the material (i.e. not just in mounds on a flat floor).

Landfarming

Landfarming techniques were developed for remediation of terrestrial sandy soils. The material is spread out in layers on specific areas. Ploughing the soil stimulates the diffusion of air, necessary for aerobic degradation. Compared to terrestrial soils, dredged sediments have a high moisture content and smaller particles. The first phase of landfarming a contaminated dredged material, therefore, consists of dewatering by evaporation and drainage (see Section 3.1.1), and ripening (development of soil structure as opposed to slurry). At this stage air can penetrate and degradation commences. Three landfarming techniques were developed under the Dutch POSW, intensive, intrinsic and greenhouse farming.

Intensive Landfarming

This is an outdoor technique originating from the remediation of terrestrial sandy soils. Legislation prescribes measures to prevent emissions to soil and groundwater, a protection layer (HDPE-foil) and a drainage layer combined with a collecting system for the water.
The first project started in 1989 with 500m^3 from Zierikzee Harbour and Geul Harbour and ran for four years.

Intrinsic Landfarming

When intensive landfarming has reached the second phase of bio-remediation degradation is limited by sorption of pollutants to the sediment matrix. Measures to stimulate bacterial activity (like ploughing) are no longer effective. Degradation can only take place after diffusion (desorption) from pollutants out of the matrix. When given sufficient time (and a little effort) "rest" concentrations might be removed in a natural way (see Section 1.5.1 – natural recovery). The sediments from Zierikzee Harbour and Geul Harbour already treated by intensive farming were further treated in this way for another three years (Harmsen et al, 1997). The results showed that PAH's could be reduced further. Extrapolation of the trends suggested a total residence time of 11 years would be needed for Geul sediment and 40 years for Zierikzee sediment.

Greenhouse farming

This takes place indoors and is faster due to control of heating and aeration. One trial indicated that the process of degradation was about 4 times faster (Ferdinandy-van Vlerken, 1997).

When sediment is treated in a landfarm, the soil is spread out in layers of 0.3 to 1.5m and moisture content is usually kept at 80%. Sometimes fertiliser is added to provide nutrients for the microorganisms and the land may be ploughed in order to improve the soil structure. A loose structure is necessary to allow oxygen penetration. The results of an experiment in treating PAH's are shown below. The sediment had already been treated by removal of the finer fraction by hydrocyclone and the treatment was applied to the more sandy "underflow" material. After 190 days low concentrations of the lighter polycyclic hydrocarbons can be reached but benzo(a)pyrene does not decrease at all.

Table 3.13 PAH biodegradation in Geulhaven sediment under optimal landfarming conditions (Van Dillen, 1991)

PAH	Concentration mg/kg dry solids				Efficiency
	0 days	67 days	130 days	190 days	%
Fluorene	4	3	0.7	<0.2	>95
Phenantrene	16	8	4	0.7	96
Chrysene	3	2	1	0.5	83
Benzo(a)pyrene	2	4	3	1	0

Groot et al (1993) came to similar conclusions based on two field trials, one involving a sand rich sediment (> 70% sand) and a relatively silt-rich sediment (< 20% sand), in which bacterial, adapted to PAH's were added. The main conclusions were:

- Absolute reduction in PAH's of about 80% (silt rich sediment) to about 95% (sand rich sediment) were achieved;
- Relatively rapid bio-degradation of the PAH's occurred in the first few weeks, after which it proceeds very slowly;
- After about 2 years, a level was reached where the material may be reused without the need for isolation measures;
- The effect of various test conditions (addition of bacteria and soil structure enhancer) is virtually impossible to demonstrate;
- Little or no leaching of contaminants from the dredged material was found.

On the basis of the above field trials a large field was set up for cleaning about 12,000 m^3 of sediment in 1995 (Bruijckere, 1996). The material contained high concentrations of PAH's and relatively low concentrations of heavy metals. To facilitate the process, a porous, adsorbing soil protection layer was chosen as underseal instead of an impervious foil layer. This is because the field experiments showed that the dredged material is difficult to drain. This means that the sediment remains wet too long to achieve effective biodegradability, as the presence of moisture impedes the supply of sufficient oxygen. Laboratory test had shown that a soil protection layer consisting of a mixture of sand and peat (10% peat by weight) offers sufficient protection for the underlying soil and groundwater, and is even better than a foil layer (Harmsen, 1995). The peat adsorbs any leaching of pollutants while there is no obstacle to the natural drainage of the dredged material. The results of these trials, expected to take at least two years, are not available at the time of writing.

DARAMEND^R

DARAMEND is a bio-remediation technology based on the landfarming technique. IT was developed under the sponsorship of the Government of Canada. GRACE Bio-Tech possesses the license for world-wide application (Bucens and Seech, 1997).

DARAMEND is often applied as a form of landfarming to 0.6m deep lifts. The aerobic biological technology utilises organic (DARAMEND) products and inorganic (i.e. nutrients, pH modifiers) amendments to optimise the activity of micro-organisms indigenous to a soil ore waste, resulting in natural destruction of organic contaminants. DARAMEND are soil-specific solid phase organic amendments that alter the physical and chemical properties of treated waste to enhance biological activity. For each soil DARAMEND is designed to a specific particle size, with a specific nutrient profile and nutrient release kinetics. No microbial inoculation is required.

Demonstration tests were carried out on two Lake Ontario sediments, Thunder Bay (contaminated with creosote) and Hamilton Harbour (coal tar and heavy metals). In both studies, following addition of 8% by weight or less DARAMEND amendment the concentration of PAH's was significantly reduced. In the Hamilton project they were degraded from about 1000 ppm to 100 ppm in 300 days. In the Thunder Bay studies the reduction was from 570 to 70 ppm in 113 days. The majority of the decrease occurred in the first two months. The concentrations of both high and low molecular weight PAH's was shown to decrease (i.e. 4 to 6 ring PAH's decreased by 83% in Thunder Bay sediment). Further, radioisotope tracer studies demonstrated that mineralisation to carbon dioxide was a key fate of the PAH's.

FORTEC^R

The Fast Organic Removal Technology is biodegradation of organic contaminants integrated with soil washing (see 3.2.5.4). Heavily contaminated sediment from a port was selected for trials (oil concentration 10,000 – 30,000 mg/kg, PAH 1000 – 3000 mg/kg). Full scale trials involved the treatment of 3000 tonnes of the sediment. The contaminants were first concentrated into the fine fraction by a separation technique. The sandy fraction (65% of solids) required only an additional step of flotation to meet Dutch target levels. The fine fraction was treated in a series of bioreactors. Within an overall retention time of 8 days more than 80% of both PAH and mineral oil had been degraded.

In the full scale tests the pH was controlled at neutral pH (pH 6.8-7.0), a higher pH was not possible. The temperature was set at the desired level of 35^0C. The oxygen level was continuously maintained above a minimum level of 2mg/l.

3.2.7.3 Composting

Composting is a biological treatment process used primarily for contaminated solid materials. Bulking agents (eg wood chips, bark, sawdust, straw) are added to the solid material to absorb moisture, increase porosity and provide a source of degradable carbon. Water, oxygen and nutrients are needed to facilitate microbial growth. Dewatering will often be necessary as a pretreatment step before composting. Available techniques include aerated static pile, windrowing and closed reactor designs (USEPA 1991d).

Volatilisation of contaminants may be a concern during composting and may require controls such as enclosures or pulling air through the compost pile rather than pushing air into and out of the pile. Use of composting to treat sediments should increase permeability of the sediment, allowing for more effective transfer of oxygen or nutrients to the microorganisms. A pilot scale demonstration of composting was conducted for Environment Canada's clean-up fund at a site in Burlington, Ontario. Approximately 150 tonnes of PAH-contaminated sediment from Hamilton Harbour were placed in a temporary shelter and tilled periodically with additions of a proprietary organic amendment (Seech et al, 1993).

3.2.7.4 Contained treatment facility

Confined disposal facilities, normally used to isolate contaminated sediment, may also be used as treatment facilities for bioremediation. However, the size of the CDF and the depth (1.5 – 5.0m) of sediments may limit the capability to control conditions compared to other systems. A schematic layout is shown in Fig 3.10. A pilot evaluation of such a facility for PCB contaminated sediments is underway at the Sheboygan River AOC. Rather than a dyked facility the containment is provided by sheet pile walls and includes an under-drain system that can be used for leachate control and to add nutrients, oxygen and other additives.

3.2.7.5 Biofixation

Although the use of bio-augmented bacteria is now well developed the effectiveness of such treatments is subject to certain constraints. These can be overcome by the use of biofixation, enabling resolution of problem cases previously considered difficult or impossible to treat.

Early tests on biofixation arose because of some of the problems encountered in biodegradation, especially with in situ treatment where conditions are frequently anaerobic due to the presence of organic matter. Anaerobic degradation is a slow process even when working with carefully selected bacteria. Complex compounds such as PCB's or high concentrations of metals limit degradation potential. The biofixation product consists of a mineral carrier on which bacteria are fixed together with essential nutrients. The necessary oxygen for the start of the treatment is delivered by this carrier which is extremely porous. Early tests carried out in Belgium showed promising results. In situ tests were inconclusive but ex situ tests showed 80% reduction of PCA's after 3 months while the amount of toluene doubled in the same period resulting from the degradation (Kreps-Heyndrikx and De Fraye, 1991)

Biofixation is based on the principle of chemi-osmoregulation. It depends on fixing selected strains of micro-organisms to carefully chosen mineral supports. The combination of micro-organisms and support gives the micro-organisms superior capabilities to activity, toxin resistance and reproduction, greater than both free living and bio-augmented micro-organisms. The TBA (Techniques et Biochemie Appliquees – known as TBA – Unisymbiose) have developed techniques to fix aerobic and facultative aerobic bacteria and fungi to solve a wide range of treatment problems including sludge, soil and silt (BCT undated)

Broadly speaking, two types of action take place, physico-chemical and biological. They provide powerful synergetic effects.

Physico-chemical

- The ionic effects of the mineral support

These take particles out of uniform suspension by coagulating them (displacing the zeta potential of the colloids). This leads to a coagulation of organic material around the biofixation particles, drawing the pollutant elements towards the biofixations.

- Adsorption

Adsorption of ammonium, hydrogen sulphide and mercaptans by the specific porosity of certain minerals in the biofixations, and by their crystalline structure.

- pH buffer

Biofixation dampens tendencies towards the acidifying and alkalising of the water, as the mineral support acts a d a buffer reducing pH changes in the water. Naturally, in the case of extreme acidity or alkalinity, preliminary rectification will be necessary.

In the pores of the biofixation, micro-climates independent of the external environment are created, protecting the micro-organisms from the toxins. This is particularly important during the biological action of the nitrification process, during which acidification occurs, and inhibits the reaction. The buffering of the pH in this instance accelerates the oxidation of the nitrogen.

- Ion exchanges

Aided by the oligo-elements in the mineral support, the complex chemical balances created in a charged aqueous environment will regulate the formation of certain undesirable ionic concentrations.

- Blockage of metals

The potassium silico-aluminates in the mineral support will block certain harmful metals due to an exchange of potassium ions for metallic ones in a preferential sequence (See Table 3.14). This neutralises the charges on the metal ion and renders it inactive. The different metal ions are, in preferential order of uptake:

Table 3.14 Order of uptake of metal ions

Cobalt	=>	Arsenic	=>	Cadmium	=>	Lead
Copper	=>	Chromium	=>	Iron++	=>	Iron++
Antimony	=>	Silver	=>	Caesium	=>	Strontium 90
Uranium	=>	Vanadium	=>	Mercury	=>	Nickel
Zinc	=>	Titanium	=>	Tin	=>	Gold

Once the metals have been blocked, the natural degrading process will be enhanced because their toxicity to micro-organisms has been neutralised. The metals cannot be eliminated as they are not degradable, but they will no longer be found in solution and will be less problematic in the sediment. Essentially, once locked in the crystals, they will not be dissolved by the water, even if highly acidic.

- Precipitation

Certain elements are precipitated out of solution by the ionic exchanges catalysed by the Biofixation, eg soluble phosphates become tricalcic phosphates or ammonia-phosphate calcics.

This means that the different micro-organisms obtain priority access to those pollutants which also act as nutrients. Eg in the case of nitrogen and phosphorus deficiencies, the growth and competitiveness of bio-fixed micro-organisms will be preferred.

Biological

The bacteria chosen and fixed to the mineral support have been selected because of their appetite for certain pollutants:

- Degradation of chemical micro pollutants

Hydrocarbons, animal and vegetable fats, phenols, halogenated organic compounds are largely undegraded by the natural bacteria present in the aquatic environment. If present, even in small quantities, they tend to limit the activity of the natural flora, disturbing transfer of oxygen and slowing the settling process. Their elimination leads to an enhancement of the working of natural flora.

- Resistance to toxins

From within their support, the bacteria are better able to tolerate certain toxins. Biofixed bacteria have been shown to survive exposure to chlorine concentrations as high as 250 mg/l, when biofixed compared to the usual 1mg/l considered fatal. Biofixed bacteria are also protected from UV radiation.

- Virility

The speed of reproduction and enzyme production is greater for biofixed than for "free floating" bio-augmented bacteria, due to the chemi-osmoregulation operating within bacterial membrane and the support. This process facilitates all bacterial transmembrane hydrogen ion movement.

- Nitrification

In theory the nitrification process, partly involving the conversion of ammonia to nitrates, takes place when organic matter is almost completely oxidised. More importantly, this process is quite slow given the low reproduction rates of nitrifying bacteria. As the biofixations incorporate large colonies of bacteria, both parts of the nitrification process are enhanced and nitrification will take place considerably faster.

- Competitiveness

The bacteria fixed on their support will be preferred against obstructive bacteria (eg filamentous ones) in their competition for nutrients. Filamentous bacteria, though quite good at degrading wastes, impede the flocculation process by meshing if they are present in high concentrations. Their membrane surface enables them to perform even in areas of low nitrogen, phosphorus etc., but not as well as biofixed ones, which are protected within their support and have nutrient sources close by. The elimination of foam on aeration basins and clarifiers takes place at the same time as the biodegradation of micro-pollutants such as grease, and by the competitive inhibition of filamentous bacteria, especially Noccardia.

- Sludge quality

Biofixed bacteria have a powerful degrading action on organic matter, especially on substances difficult to degrade naturally, and can thus increase the oxidation activity in the sludge. This tends to increase or maintain a positive redox potential, and thus its ability to use the oxygen present to degrade organic, carbonised or nitrified matter.

BCT offer a number of products to deal specifically with certain contaminants. As far as we are aware they have not been used to treat dredged material specifically but have been used in soil remediation.

The advantages and disadvantages of most of the bioremediation technologies are summarised in Table 3.15.

Table 3.15 Summary of bioremediation technologies (USEPA 1994)

Technology	Advantages	Disadvantages
Bioslurry treatment	• Offers most control of the physical/chemical environment. • Easy to monitor effectiveness. • Enclosed reactors can capture fugitive volatile emissions • Provides highest biological reaction rates. • Offers capability to treat the broadest range of organic compounds and sediment types. • Treatability testing and engineering scale-up is relatively simple.	• Considerable energy may be required to keep solids in suspension (thereby increasing cost). • Potential materials handling problems may require significant pretreatment. • Equipment intensive compared to other bioremediation options – operation and maintenance of system is a critical component.
Contained Land Treatment	• Reduced operation and maintenance required compared to bioslurry systems. • Leachate collection system minimises groundwater impacts. • Treatment in an enclosure allows more environmental control and opportunity to collect and treat volatile contaminants. • Less energy intensive than slurry systems.	• Sampling and analysis to verify treatment effectiveness more difficult compared to bioslurry systems. • Leachate collection and treatment for sediments will complicate system operations and add to costs. • Operational control to optimise biotransformation somewhat difficult to maintain. • Large surface areas required for this lifts of sediment. • Sediment moisture adequate initially, but irrigation may be required as evaporation and drainage progress.
Composting	• Reduced operation and maintenance compared to bioslurry systems. • Added bulky organic materials enhance biotransformation and improve permeability of sediment, which provides for improved control of environmental conditions in the compost pile. • Static piles can be quite thick, requiring less land area compared to contained land treatment. • Produces material suitable for a wide array of beneficial	• Control of volatile emissions requires enclosure or innovative aeration techniques. • Source of bulking agent required. • Materials handling problems may develop in mixing and placing wet sediment in compost piles.

	uses.	
Contained treatment facility	• Under favourable conditions, offers lowest cost. • Although the reaction rate is lowest, a large volume of sediment may be treated at once. • Favours anaerobic processes, which show promising results for reductive dechlorination. • Materials handling of sediment and rehandling of treated material is relatively easy.	• Applications limited to favourable sediment characteristics, such as coarser materials with high permeability. • Extensive treatability studies, sediment characterisation and site information required. • Leachate control may be necessary. • Difficult to monitor clean-up efficiency. • Difficult to transport oxygen, nutrients or other amendments through fine-grained sediment with low permeability: significant pumping and drainage system may be necessary.

3.2.7.6 Plant cultivation

A completely different technique is decontamination using plant cultivation (Detzner 1993). This method uses the capacity of various plants to collect substances (such as heavy metals) through their root system or directly through the cell walls of algae. The results depend on the soil characteristics, the mixture and concentration of contamination, and the plant's ability to absorb contaminants.

Bush and tree farming

The use of willows is suggested by Ferdinandy – van Vlerken (1997). Willows will optimise the structure of the material and can be burned for energy supply afterwards.

In the Netherlands it is estimated that about 10% of the total amount of contaminated sediments produced up to the year 2015 will be suitable for biological cleaning. By setting up a vegetative land farm, this quantity can be extensively cleaned. Vegetative land farming can be summarised as follows (Bruijckere, 1996):

- The contaminated sediments are applied to a prepared terrain (eg about 100 hectares) in a layer no more than 0.8m thick:
- The right conditions for biodegradation are created, especially good aeration and the necessary water and food regime, so that most of the pollutants are broken down in about 2 years;
- Selected bushes and trees are then planted to improve the structure of the ground so that bio-degradation can continue, although more slowly;
- In this way, after 10 – 20 years, all pollutants will have decomposed or will have transformed into harmless compounds. A properly functioning ecosystem will have developed in and on the soil.

Fungi Farming^R

Complex compounds such as PAH can be degraded in a few months by means of a fungi. Reductions of 65 – 95% have been achieved. The method works well in various circumstances such as low temperatures and dredged material with a high clay content. In addition to PAH mineral oil proves to degrade in a short period by 90-95%. The time scale seems to be much shorter than more traditional landfarming.

Plants and trees produce lignin that becomes part of the skeleton of the wood. Lignin is a biopolymer with an irregular aromatic structure. A small group of organisms, the white rot fungi, is capable of mineralising the lignin. This is based on the precipitation of specific enzymes such as lignin peroxidase and manganese peroxidase and enzymes that produce hydrogen peroxide. In this the fungi can be distinguished from bacteria that are not capable of biodegrading lignin in this way.

Many experiments have been carried out with white rot fungi such as *Trametes versicolor, Phanerochaete chrysosporium* and *Bjerkandera* species to degrade lipophilic pollutions such as PAH, since these have a structure that resembles lignin. Field's experiments proved that white rot fungi that precipitate peroxidases are capable of degrading PAH's. Research by DHV (van der Kooij 1997) showed that other fungi are also capable of degrading PAH's.

The results of the DHV research are shown in the Table 3.16.

Table 3.16 Fungi farming – results of experiments

Conditions	**Period of stay (days)**	**Final result**		**PAH reduction %**	
		PAH (in VROM) mg/kg	**Category**	**VROM series**	**EPA series**
Sandy/peat dredge material, PAH 35 – 40 mg/kg, *Agaricus bisporus*					
Blank outdoors	80	43	3	nil	nil
In winter in open air	80	8	2	79	79
In winter under glass	80	11	2	71	71
Indoors	80	9	2	75	76
Old compound manure, indoors	80	6	2	83	83
Blank indoors	80	23	3	35	36
In spring in open air	55	8	2	76	77
Indoors	55	13	3	64	63
Dredged material rich with clay, PAH 75-100mg/kg, *Coprinus comatus*					
Blank in open air	90	69	4	nil	nil
in open air	90	15	3	83	84
in open air	90	2.5	2	>95	>95
outdoors under foil	90	12	3	84	86
outdoors under foil	90	7	2	93	93
Heavily polluted dredged material, rich with clay, PAH c1200 mg/kg, *Coprinus comatus*					
Blank in open air	90	195	4	83	81
in open air	90	33	3	96	96
in open air	90	18	2	96	97
outdoors under foil	90	49	3	94	95
outdoors under foil	90	43	3	91	91

It was concluded that not only peroxidase enzymes are capable of degrading PAH's. The fungi technology offers good possibilities of in-site treatment of polluted dredged material, especially if waste compound manure of commercial fungi growth can be used.

3.2.7.7 Biotechnological leaching

Leaching metals from ores using bacteria is a well-known method but it has some limitations. Many micro-organisms produce chelators with which they mask hazardous metal-ions to defend themselves.

Lactic acid can be produced by many bacteria, in high amounts and rather efficiently. Lactic acid is a strong organic acid and a strong chelator of heavy metals, which means that re-sorption and precipitation of the dissolved metal can be prevented. The choice for lactic acid instead of citric acid is made because sediments are very anoxic and lactic acid is produced at a more negative redox-potential than citric acid.

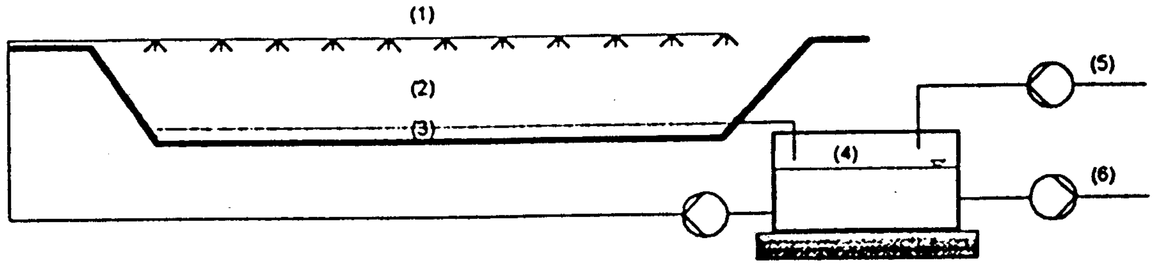
When the bulk of the metals has been dissolved by the lactic acid, oxidation of the persistent metal sulphides starts by Thiobacilli ssp. These are chemo-litho-autotrophe, which means that they grow slowly and have a slow metabolism. So they have got a place in the process where all the easier soluble metal compounds have already been removed.

Thioleaching

Thioleaching is a recognised method in the Netherlands (Seidel et al 1997, Rienks 1997). It uses micro-organisms of the genus Thiobacilli to produce sulphuric acid by oxidation of sulphides or added sulphur. Because of the change in redox potential and the scouring by sulphuric acid, heavy metals are dissolved. Using a mixed culture of Thiobacilli and acidophilic micro-organisms could lead to degradation of organic compounds like mineral oil and PAH's.

The results of laboratory experiments showed 70-75% removal of heavy metals, with the exception of lead and arsenic. The degradation of mineral oil and PAH varied considerably. The removal of individual PAH compounds was identical, which does not indicate biodegradation. On the contrary, not inoculated reference experiments did not show any significant removal of mineral oil and a smaller decrease of PAH. The conclusion was that much research would be needed to elucidate the fundamental aspects of this possible treatment process (Rienks 1997).

Suspension leaching is not practical for large amounts of dredged material. One alternative would be percolation leaching similar to the dump leaching used for ores. A diagram showing such a leaching plant at pilot scale is shown in Fig 3.13.



(1) Sprinkler	(2) Sediment	(3) Drainage
(4) Tank for leachate	(5) Fresh water, chemicals	(6) To leachate treatment

Figure 3.13 Leaching pilot plant

BiMicrobial Metaleaching^R

This has been developed by SEC (Storm Environmental Consultancy) (Storm van Leeuwen, 1991). It is based on the concept of optimising metabolic circumstances for micro-organisms and keeping them off balance. The process technology developed for leaching of heavy metals consists of a series of reactors in which steep gradients are carefully kept, on a macro and on a micro scale. Only when a gradient is no longer sustainable, a new cycle is started to impose a new steep gradient and so on. Even the cycles themselves form a gradient. Starting neutral (pH 7), the acidity of the silt suspension increases in each cycle until pH 1 is reached.

In the Membrane Reactor^R a continuous gradient is kept in dry matter content across the central membrane, in order to carry away the dissolved and chellated metals. This gradient is enforced by an electric field in the same direction, in order to accelerate the transport across the membrane of the positively charged lactate chellates carrying a bivalent metal ion

When the dry matter content allows no further de-watering, a new cycle is started by mixing the silt with fresh (partly re-circulated) water with lactic acid and glucose. In this way the bacteria are not hindered by their own metabolite (lactic acid) and are not poisoned by an increasing concentration of dissolved metals.

3.2.7.8 In situ treatment

In 1992 several products entered the Dutch market for in situ sanitation or bio-degrading. The powder-like products , containing nutrients, bacteria and in some cases oxygen carriers, had to be spread over the surface water, would sink to the bottom and stimulate bio-degradation of mineral oil, PAH's and organic matter, This concept might offer a simple and cheap solution since dredging would no longer be necessary. The Dutch research programme looked into this approach (POSW, 1994) and found that no degrading bacteria or oxygen carriers were present in the products. Therefore it was not surprising that no effects of PAH or oil degradation occurred, mostly due to lack of oxygen in the sediment. Even with a mechanical system for introducing air, results were poor (Geradts, 1996).

Generally the chances for in situ aerobic bio-remediation are judged to be very low, since more effective aeration would lead to dispersion of contaminated sediment into the water system (Ferdinandy – van Vlerken, 1997).

Attempts at in situ clean up in the old fish harbour of Zeebrugge (Belgium) were disappointing, which was attributed to oxygen deficiency, and alternative ex-situ treatments had to be considered (De Brabandere et al 1997).

Nevertheless at least one technique is reported as being reasonably successful. BIO-C^{TM} was developed by HAECON in 1988. The treatment was formerly known as ABR-CIS. It is designed for the removal of organic material, particularly mineral oils in order to deal with smell nuisance in canal sediments, where the natural equilibrium is disturbed due to the accumulation of contaminants and where oxygen concentration is not sufficient for aerobic degradation (Meyer et al, 1996).

The basic principle is to deliver oxygen to destroy organic contaminants in situ in waterways by means of augmented aerobic biodegradation processes. This can be attained by conditioning of the sediment combined with the addition of specific micro-organisms if needed. This conditioning is performed with microcrystalline natural minerals in which micro-bubbles are trapped, and progressive release of oxygen in the environment wherein it is injected.

Depending on the environment to be treated BIO-C^{TM} can be enriched with specific micro-organisms selected with regard to the contaminants to be biodegraded.

The equipment consists of a series of steel tubes mounted in parallel on a supply-pipe at a relative distance of 0.5m. Each tube is fitted with discharge holes. The diameter of these holes can be modified according to the physical characteristics of the sediments. The discharge of BIO-C^{TM} suspension flows perpendicular to the injection pipes. The intensity of the stream and discharge is controlled from a pressure tank containing the suspension. Heavy weight metal chains at the end of the pipes assures final mixing of the sediments with the suspension. The injection device as described is towed by a tugboat.

Continuous injection is performed while navigating at a cruising speed calculated according to the physical characteristics of the sediment. In the case of treatment of the Moervaart sediments it took 13 days to inject 13,000m^3 of sediment.

The sediment changed colour approximately one year after treatment. Originally the sediment was black, changing to a light grey colour as oxidation took place. After biodegradation of the mineral oils, together with the reduction of the concentration of sulphides, the odour perception value (Threshold Odour Number) decreased significantly. The concentration of mineral oils was reduced by 97% leaving no more than 200 ppm remaining in the sediment. The concentration of free sulphides was reduced by 70%.

3.2.7.9 Zeebrugge case study

Different ex-situ microbial remediation techniques were assessed for the clean up of contaminated sediments in the old fish harbour of Zeebrugge (De Brabandere et al 1997). Sediment contamination typically consisted of PAH's (5 to 1200ppm), TBT (up to 400ppb) and mineral oils (400 – 800ppm). In a first bench scale phase the remediation efficiency of techniques based on stimulation of indigenous bacteria and/or three commercially available strains was evaluated using a combination of kinetic, ^{14}C and respiration experiments, aimed at determining the degradation pathways and overall fate of the contaminants. At a pilot scale 3 selected remediation techniques were assessed in four 40m^3 batch reactors (second phase). Aquatic toxicity tests were used to monitor bioremediation efficiency and the potential hazard of water and remediation by-products. The results for both phases of this study indicate that selected ex-situ microbial remediation techniques of contaminated sediments can remove 90% of both mineral oils and TBTs and between 70 – 90% of total PAH concentration.

About 50m^3 was dredged out of the fish harbour at 40 different places throughout the contaminated zone. It was transported to the treatment facility. After sieving and mixing it was equally divided over 4 bioslurry reactors of 50m^3 each. The first phase of the treatment consisted of stimulation of the indigenous bacteria by oxidising the sediment with addition of fertilizers. After about 6 weeks 3 out of 4 of the reactors were inoculated with selected organisms according to the selected procedures from the previous phases. After 6 months of treatment the reactors were emptied. The sediment was allowed to settle in specially designed lagooning fields. These enabled a natural and quick dewatering of the sediment (2 weeks). When the lagoon was sufficiently dewatered the sediment was further treated with landfarming techniques. The pilot scale treatment was intensively monitored by ecotoxicological tests.

The bench scale tests showed that in most cases the sediment can be conditioned to act as a battery system for maintaining the essential aerobic conditions for degradation of organic compounds. It also appeared that complete oxygen saturation enhanced the degradation. The use of surfactants proved not to be essential whereas the exact dosage of nitrogen and phosphorus was more influential.

During the ^{14}C tests a shift from dichloromethane extractable ^{14}C to non-extractable ^{14}C for the labelled molecules was observed. Further analysis revealed that the non-extractable ^{14}C was associated with the humines. The amount of ^{14}C recovered as ^{14}C-CO$_2$ was 10% for benzo(a)pyrene and 54% for naphthalene. The results were not influenced by adding microbial inocula. Results of GC-MSD measurements indicated an overall removal efficiency of 70% after 7 weeks (half life: 1 month). The expected yield of the treatment based on the bench tests were:

Mineral oils	90%
PAH	95%
TBT	90%

High weight PAH reduced from 9.5 to 1.5ppm

Pilot scale testing showed that oxygen saturation could be kept sufficiently high to a depth of more than 2.5m even after a (simulated) power failure of 4 hours. Biodegradation was monitored for mineral oil, TBT and PAH. This revealed a difference between the indigenous and inoculated systems. The latter showed particularly better degradation of the higher molecular weight PAH's and a distinct better overall degradation yield.

The use of indigenous stimulation accounted for at least 60% of the degradation. The use of extra microbial blends if properly applied can improve the results. The use of surfactants may be required whereas appropriate fertilizing is essential.

3.2.8 Electrokinetic technology

Electrokinetic treatment is a technology used in remediating contaminated soils and sediments. The method can be used to extract inorganic substances, such as heavy metals, from the contaminated soil. In electrokinetic treatment, passing a direct electric current through the soil drives contaminant transport. The current causes substances that are present as ions in solution to migrate towards the oppositely charged electrode. The theory is that contaminants transported in this way will be deposited at the electrodes which can then be removed and suitably disposed of or recycled.

World-wide, there are only a few case studies of using electrokinetics for remediation of contaminated land and no cases were found concerning in situ remediation of sediment, other that the trial for remediation of mercury contaminated canal sediments reported in Appendix 1 (CIRIA, 1998).

Electrokinetic treatment is used to separate and extract heavy metal and organics from soils. The treatment process can be applied in situ or ex situ. Application in situ has the advantages of reduced costs, limited physical disturbance of the waterway and lower human exposure to the contaminated sediment.

Electrodes are inserted into the sediment at prescribed distances apart to apply a voltage and pass DC current through the sediment. A number of processes result from this. The ions become aligned in solution followed by their mobilisation and transport to the electrodes where they deposit.

During mobilisation and transport, contaminants are removed from the sediment by two processes, electro-osmosis (EO) and electro-migration (EM). Electro-osmosis is a process whereby the soil particles in the system remain stationary and the water (pore fluid) is transported in the direction from the anode to the cathode. Water molecules are dipolar and some water therefore will also be transported to the anode. The pore water will migrate as described above and the ions (heavy metals), colloids (behaving like ions) and soluble complex salts dissolved in the water will migrate towards the electrode bearing the counter charge.

The concurrent mobility of the ions and the sediment mass to the electrodes where the contaminants are deposited. The order in which the contaminants are deposited at the electrodes depends on their position in the periodic table.

Electrode selection is important in the electrokinetic process because it has implications of the effectiveness of the treatment as it affects the plating process at the electrodes. In addition, care needs to be taken over the selection of the electrodes, as some metal anodes will dissolve as strong oxidants are formed at the anode during the process.

The extent of removal of contaminants from sediments that are strongly sorbed (attached to the sediment particles) is not known. As the contaminant ions move towards the electrode, the concentration of metal ions in the sediment moisture decreases, but is further restored by exchange with the soil phase. These ion displacements and ion exchange will continue while the electric field is maintained. Therefore, some desorption of contaminants is expected to occur in the process but it is likely that a residual concentration of contaminant in the soil or sediment will remain as contaminants form strong associations with sediments. An important parameter for electrokinetic remediation is the cation exchange capacity (CEC).

This gives an indication of the mobility of the cations attached to the sediment particles. To improve contaminant mobility, it may be necessary to mix the sediments with different acidic or, depending on the contaminant, alkaline solutions. In addition, conditioning fluids may be added or circulated at the electrodes to control the electrochemical process. This is likely not to be possible for the in-situ remediation of sediments because the volumes of additives likely to be needed and the potential implications on water quality and surrounding ecology.

The contaminants will be deposited onto the electrodes in a preferential order depending on the contaminant reactivity. Deposition of heavy metals, colloids and complexes on the electrodes is governed by Faraday's Law. The order in which the contaminants will plate out on the electrodes depends on their position in the periodic table and is termed the Galvanic Series. For example, copper will be deposited out before mercury.

Electrokinetic processes are also reported to mobilise and transport polar organic compounds (such as phenols) as well as organic colloids and organic ions. These substances will not deposit on the electrodes but will be transported towards them. The potential of the process to cause uncontrolled mobilisation of harmful organic substances is important as it may cause contamination of the waterway and be detrimental to the aquatic ecology.

It should also be noted that the distribution of heavy metals in various types of bonding (see Section 2.2.1) is a result of a series of interconnected equilibria between various types of bonding (Kliem et al 1997). Changing the amounts of heavy metals in any of these will displace the equilibria. The conditions most relevant for retention of heavy metals in dredged material can be summarised as:

- The heavy metal species
- pH
- Redox potential
- size of clay fraction
- Content of organic matter
- Content of carbonates

The field trial monitored by HR Wallingford concerned a canal adjacent to the historic site of a munitions factory. The silted up canal was to be restored and surveys had shown mercury concentrations up to about 12,000mg/kg (dry weight). Unfortunately, due to some practical difficulties with site observations and a wide variance in sample analysis results, it was not possible to draw firm conclusions about the effectiveness of treatment. At the time of writing no decision has been made concerning the possibility of full scale remediation by this technique. However, the technique has many attractions and merits further investigation.

3.2.9 Natural ripening

Ripening of dredged material in a deposit is a natural drying process in which a slurry of dredged material is slowly transformed into a useful construction material. The end product can be used in earthworks provided that the characteristics of the ripened material comply with environmental standards and civil engineering construction demands. It is particularly suited to materials with a low sand content (de Haan et al 1997, Heynen et al 1997).

The material is put into a temporary deposit where dewatering and consolidation can take place. During and after dewatering oxygen is able to penetrate into the dredged material causing the oxidation of anaerobic organic matter and minerals.

Ripening is an interaction of three components:

- Physical ripening: irreversible loss of water resulting in the formation of permanent cracks (aeration) and subsidence of the surface (compaction).

- Chemical ripening: changes in chemical composition due to reactions and leaching of soluble substances during the transition from anaerobic to aerobic conditions.
- Biological ripening: changes in the culture of micro-organisms and the structure of organic material during the transition from anaerobic to aerobic conditions.

Physical ripening can be regarded as the driving force for the whole process. Control of the dewatering process is already described in Section 3.1.

Experiments are in progress in the Netherlands to try to optimise the management of ripening. The main activity is a monitoring programme involving regular sampling and analysis of the material. The results so far indicate:

- A layer thickness of 1.0m of dredged material can be processed to soil useable in earthworks during a single spring-summer season.
- Reduction of PAH (the main contaminant of concern in the test material) due to biodegradation had not been observed (however, see Zeebrugge case study Section 3.2.7.9).
- Mineral oil contamination reduced by about 45%, mainly achieved during the summer.
- Material expected to be useable under Dutch environmental legislation for application in earthworks and landfill covers.

4. DISCUSSION

This chapter discusses the criteria for a successful technology then explores the match between contaminants to be treated and the available technology. Each of the principal criteria, effectiveness, practicality, cost and socio-political perceptions are discussed with respect to each of the technologies.

4.1 Criteria for a successful technology

4.1.1 Available

The main question to be asked will be "Is the technology commercially available or what is its stage of development?". If it is not available, does the need justify the research and development cost. This is discussed further in Chapter 5.

4.1.2 Appropriate

The technology will most likely have to remove, destroy or reduce a range of contaminants. The percentage removal of contaminants from sediments will depend on the contaminant under investigation, the contaminant concentration of the feed sediment, the operation conditions (temperature, pressure and residence time). The target residual concentrations must be determined. Usually these are set by national environmental standards applicable to the final destination or use intended for the treated material. Sediment properties, such as percentage fines (<63μm) and organic matter will affect the decision because these in turn affect the degree of adsorption and strength of the bonds. Often a chain of treatments, including pre-treatment, will be necessary.

4.1.3 Practical

The decontamination technology must be practical. Volumes of dredged material to be treated are likely to be high, therefore, process capacities will need to be high and the residence time of the process must agree with the projects overall timetable. Few people correctly conceive the scale of the problem. There is little point in setting up a batch processing plant capable of handling a few kilograms of material per hour when a trailing suction hopper dredger might be delivering 2000 tonnes of contaminated material each dredge cycle.

4.1.4 Effective

The most recognised method for assessing the effectiveness of a decontamination technology is by using removal efficiencies and residual contaminant concentrations. Ultimately, the effectiveness will be measured by the ability of the decontamination technology to alter the material properties sufficiently to render it suitable for beneficial use or safe disposal.

4.1.5 Cost effective

The technology must be cost-effective compared to alternative options. In accordance with the principles of sustainability the costs and benefits should include environmental costs and benefits, recognising that these cannot always be expressed in financial terms.

4.1.5.1 Comparing clean-up costs with alternative disposal options

It will be necessary to compare predicted treatment costs with costs of other options (open water capping, confined disposal facilities) and beneficial use projects. It is likely that controlled disposal of highly contaminated dredged material will involve the greatest costs and this may be a useful marker to compare against predicted costs of decontamination operations. Some figures are given for general guidance in Section 4.3

4.1.5.2 Financial costs and benefits to be considered

- "Pioneering" costs of development
- Capital installation of plant;
- Transportation of material to treatment site;
- Pre-treatment:
- Land purchase/rent:
- Storage facility construction:
- Energy;
- Additives;
- Post treatment;
- Final disposal of treated material (may be a benefit if the material can be recycled);
- Disposal of any resulting residues and effluents;
- Dismantling;
- Monitoring; during and after work;
- Administrative and management costs (including those associated with obtaining permits);
- Taxes (eg VAT and environmental taxes in various forms).

Questions to be asked include; "will it be more cost-effective to transport the contaminated dredged material to the plant or to have a portable plant and take it to the contaminated dredged material?"

Overall the costs will depend on the technology, contaminant load reduction required, water content and operational conditions.

4.1.5.3 Environmental costs

These include the transfer of contaminants to other matrices (air, water) and the generation of other waste material with potentially acute levels of contaminants. Controls exist under legislation. Air emissions are controlled for certain contaminants. In removing the contaminants from the dredged material an effluent or waste cake may be generated and need to be dealt with. Process water must meet standards for effluent quality discharged into watercourses or the sewage network.

4.1.5.4 Environmental benefits

The main benefit is the solution to the problem, i.e. the cleaning up of a contaminated area of concern and the meeting of some environmental standard.

Some technologies reduce contaminant loads permanently and beneficial use of the dredged material may be possible.

4.1.6 Socially acceptable

Public intervention is playing an increasing role in decision making and dredging activities are no exception. Dredged material needs to be seen as a resource not as a waste and the products will have to be regarded as acceptable and marketable.

Environmental acceptability and public perception are increasingly important. The location of decontamination plants at some sites may be unacceptable to the public (the NIMBY-Not In My Back Yard- syndrome).

4.2 Appropriate, effective and practical

From the foregoing information it is clear that there is no simple remedy covering all contaminants and it is important to match the technology with the particular application and the particular contaminants to be treated. This section provides some guidance on the factors that must be considered in making the selection.

4.2.1 Target contaminants

Selection of the treatment technology for a particular contaminated sediment site should first determine the contaminants of concern and then rate the effectiveness of each technology in destroying, removing or immobilising them. Table 4.1 reproduced from USEPA (1994), rates the effectiveness of each of the major types of technology on organic and inorganic compounds typically found in sediments. For many contaminant/technology combinations, the effectiveness has been determined, however, as the Table notes, in some cases the effects are not known or the process is only partially effective. A note is also given where a technology may increase contaminant loss for a non-target contaminant present in the sediment. When both organic and inorganic contaminants are present in the sediment more than one technology may be required to accomplish clean sediment objectives.

Table 4.1 Selection of treatment technologies (USEPA, 1994)

	Organic Contaminants					**Inorganic contaminants**		
Treatment technology	**PCBs**	**PAH's**	**Pesticides**	**Petroleum Hydro-carbons**	**Phenolic comp'ds**	**Cyanide**	**Mercury**	**Other metals**
Conventional incineration	D	D	D	D	D	D	xR	pR
Innovative incineration	D	D	D	D	D	D	xR	I
Pyrolisis	D	D	D	D	D	D	xR	I
Vitrification	D	D	D	D	D	D	xR	I
Supercritical water oxidation	D	D	D	D	D	D	U	U
Wet air oxidation	pD	D	U	D	D	D	U	U
Thermal desorption	R	R	R	R	U	U	xR	N
Immobilisation	pI	pI	pI	pI	pI	pI	U	I
Solvent extraction	R	R	R	R	R	pR	N	N
Soil washing	pR	pR	pR	pR	pR	pR	pR	pR
Dechlorination	D	N	pD	N	N	N	N	N
Oxidation	N/D	N/D	N/D	N/D	N/D	N/D	U	xN
Bioremediation	N/pD	N/D	N/D	D	D	N/D	N	N

D	Effectively destroys contaminant
R	Effectively removes contaminant
I	Effectively immobilises contaminant
N	No significant effect
N/D	Effectiveness varies from no effect to highly efficient depending on type of contaminant within each class.
U	Effect unknown
p	Partial
x	May cause release of non-target contaminant

The following sections discuss the state of the art of each of the technologies described in this report.

4.2.2 Natural recovery and in situ treatment

Natural recovery is of limited effectiveness in preventing contaminant release into the ecosystem because this approach depends on natural processes of burial by sedimentation and contaminant destruction or sequestration by physical, chemical or microbial processes.

In situ treatment using physical, chemical and biological approaches is at an early stage of development with some successes and some failures. Because of this uncertainty there are difficulties in justifying the method in a risk-based assessment of alternatives.

Whilst this report has not concentrated on the excavation and transporting of contaminated sediments it is to be noted that it is a prerequisite to all ex-situ treatment and the way the material is handled can affect its properties and subsequent treatment costs. Safety of operators is, of course, also very important.

4.2.3 Pre-treatment, separation and dewatering

The separation of solids from water is the simplest treatment process. The solids content varies with the technology used to recover them. Hydraulic dredges remove sediments in slurry form that usually requires dewatering before any other treatment can take place. The usual practice is to place material in ponds or other confined area and rely on drainage and evaporation. It is generally effective and economical but slow. The water generated usually contains contaminants which may also require treatment. Common industrial methods include centrifuge, filtration and filter presses, and gravity thickening, but these are of limited value for silt and clay sized particles.

Soil washing and particle separation are adaptations of mineral processing techniques used in the mining industry. The effectiveness of physical separation can be of the order of 90% if the contaminants selectively associate with the fine fraction of the sediment that can be isolated: further treatment of the concentrated contaminants is then required. Costs are moderate.

It is important to emphasise that separation is not an effective treatment for all sediments and does not destroy contaminants but concentrates them into a smaller volume. The high concentration residue may then be treated using one of the other technologies.

Separation is particularly applicable where the contaminants are predominantly associated with fine-grained material that is a small fraction of the total solids.

The technology is mature.

It can be used to reprocess material stored in contained disposal facilities in order to partially restore capacity.

The main limitation is that a significant proportion of the material must be sand (eg 25%) for the process to be cost effective.

Guidance on choosing the most appropriate dewatering technology is given in Section 3.1.1.4.
Physical separation methods are described in Section 3.1.2

4.2.4 Thermal technologies

4.2.4.1 Thermal destruction

Thermal destruction treatment has the advantage that very probably the target values can be achieved, however, the high water content of the sediments requires additional pre-treatment steps resulting in higher costs. It is very effective in destroying organic contaminants, including PCB's (incineration can achieve >99% destruction) however, heavy metals are not destroyed although they may be immobilised.

The main disadvantages are that they generate large volumes of exhaust gas that must be treated. It can volatilise metals, especially mercury. It increases leachability of metals in the treated solids and it can produce dioxins.

The public perception is that they understand incineration technology but there is some scepticism about its effects.

A summary of the advantages and disadvantages of thermal destruction is given in Table 3.7 in Section 3.2.1

4.2.4.2 Thermal desorption

The technologies are described in Section 3.2.3. Thermal desorption physically separates volatile and semi-volatile compounds from sediments by heating the sediment to temperatures ranging from 90 – 540^{0}C. Water, organic compounds and some volatile metals are vaporised by the heating process and are subsequently condensed and collected as liquid, captured on activated carbon and/or destroyed in an afterburner. An inert atmosphere is usually maintained in the heating step to minimise oxidation of organic compounds and to avoid the formation of compounds such as dioxins and furans. The temperature of the sediment in the desorption unit and the retention time are the most significant factors affecting performance. Heating may be accomplished by indirectly fired rotary kilns, heated screw conveyors, a series of externally heated distillation chambers or fluidised beds.

Thermal desorption processes offer several advantage over thermal destructive processes, including:

- Reduced energy requirements;
- Less potential for formation of toxic emissions;
- Smaller volumes of gaseous emissions.

The disadvantages include:

- The need for a follow-on destruction process for the volatilised organic compounds;
- Reduced effectiveness for less volatile organic compounds.

4.2.5 Immobilisation

Immobilisation alters the physical and/or chemical characteristics of the sediment to reduce the potential for contaminants to be released from the sediment when placed in a disposal site. The principal contaminant loss pathway that is reduced is leaching from the disposal site to groundwater and/or surface water.

Physical stabilisation processes improve the engineering properties of the sediment, such as compressive strength, bearing capacity, resistance to wear and erosion and permeability. Alteration of the physical character of the sediments to form a solid material (eg a cement matrix) reduces the accessibility of the contaminants to water and entraps the contaminated solids within a stable matrix. Because most of the contaminants in dredged material are tightly bound to the particulate fraction, physical stabilisation is an important mechanism. Solidification processes may also reduce contaminant losses by binding the free water in dredged material into a hydrated soil.

Chemical stabilisation is the alteration of the chemical form of the contaminants to make them resistant to aqueous leaching. Solidification & Stabilisation (S&S) techniques are formulated to minimise the solubility of metals by controlling pH and alkalinity. Anions, which are more difficult to bind in insoluble compounds, may be immobilised by entrapment. Chemical stabilisation of organic compounds may be possible but the mechanisms involved are not well understood.

The distinction between physical and chemical stabilisation is not absolute. Cement based S&S is actually a chemical treatment in which the basic process occurring is the hydration of cement. This consumes water and thickens the mix.

The main disadvantage of immobilisation techniques, and the reason why many countries do not allow immobilised contaminated dredged material to be used in construction, is that the contaminants remain in the material. It is possible that the effectiveness of the immobilisation will be short term and that leaching of contaminants will occur after a number of years.

4.2.6 Extraction technologies

These are described in Section 3.2.5. Solvent extraction gives very high removal percentages but with the soil structure being destroyed. The use of energy and chemicals is high and a concentrated contaminant/solvent stream is produced.

Solvent extraction processes are used to separate contaminated sediments into three fractions, particulate solids, water and concentrated organic compounds. Contaminants are dissolved or physically separated from the particulate solids using a solvent. Most extraction processes do not destroy or detoxify contaminants, but they reduce the volume of contaminated material that must subsequently be treated or disposed of. Volume reductions by a factor of 20 or more are possible. Most of the contaminants are transferred from the solid to the liquid phase, the latter being more manageable in subsequent treatment or disposal.

Both the solvent and surfactant can be recycled. Surfactant extraction can be preferable to solvent extraction from the environmental point of view. The drawback with the surfactant extraction process is that the recovering processes are complex and expensive. The surfactant cannot be recycled as many times as the solvent, and this reduces its applicability from the point of view of cost. Most commercial surfactants are specifically designed for solubilising generic compounds, while an organic solvent can solubilise a large spectrum of organic compounds. This is particularly important in treating matrices contaminated with a wide variety of contaminants.

The primary application of solvent extraction is to remove organic contaminants such as PCB's, volatile organic compounds, halogenated solvents, and petroleum hydrocarbons. Extraction processes may also be used to extract metals and inorganic compounds but these applications involve the uses of acids and are potentially more costly. The cost of the solvent generally is a significant part of the total cost of the process so recovery and recycling is important. Usually several extraction cycles are necessary to reduce the contamination to target levels.

Pretreatment is required to screen debris and eliminate or reduce the particle size of the material to a maximum size of about 5 mm. The water content does not have to be reduced, in fact in some cases water must be added to enable the material to be pumped.

Extraction process can operate in batch mode or continuous mode.

4.2.7 Chemical treatment

In this technology chemical reagents are added to a sediment matrix for the purpose of destroying contaminants (as opposed to extracting them). Certain immobilisation, extraction and thermal procedures also involve chemical inputs, but they are typically to alter the phases of the contaminant to facilitate its removal or binding. A clear distinction cannot always be made and some overlap exists between this and other technologies investigated.

Chemicals are typically added to contaminated sediment in batch operations in a process vessel. Chemical treatment may destroy contaminants completely, may alter the form of the contaminants so they are amenable to other treatments or may be used to optimise process conditions for other treatment processes.

Treated sediments may then be permanently disposed of or put to some beneficial use, depending on the nature and extent of residuals, including reagents and contaminants.

Chelation, dechlorination and oxidation of organic compounds are considered the most promising.

A summary of a number of technologies is given in Table 3.10 in Section 3.2.6.

4.2.8 Bioremediation

Within the period 1989 – 1997 several techniques were developed in the Netherlands from laboratory to full scale. The techniques were grouped into four concepts, treatment in situ, in landfill, in landfarms and in reactors.

Organic micropollutants PAH's, PCB's mineral oils and chlorobenzines are all amenable to biological treatment, but if target PAH concentrations are set less than 1mg/kg it will be difficult to attain with this method. The reason is that sorption of pollutants to the matrix of the sediment, results in very low degradation rates at low concentration.

Soil structure is preserved, use of chemicals and energy is low and emissions to soil and atmosphere are minimal.

High initial concentrations give high degradation rates so are more economical for removing a large part of the contaminant in a short time. Removal of remaining pollution could take place in one of the low cost intensive treatments such as landfarming.

Much progress has been made in process control and optimisation of techniques. Optimisation will have to focus on decreasing the residual concentration and reducing residence times as well as on the relations between physical and chemical properties.

Landfarming needs a large surface area as shown in the cost comparisons in Section 4.3.

Most applications to date have been for fresh water sediments containing a reasonably high percentage of sand. Additional research is needed to adapt to the contaminant mixtures, the saltwater content and the fine-grained nature of marine sediments. In addition knowledge is limited concerning the effects of contaminant mixtures, particularly mixtures of organics and metals, on biological processes.

European research appears to be much further ahead in this field than that of the USA.

4.2.9 Electrokinetic

Electrokinetic technology is used in remediating contaminated soils and sediments. The method can be used to extract inorganic substances, such as heavy metals, from the contaminated soil. Passing a direct electric current through the soil drives substances that are present as ions in solution to migrate towards the oppositely charge electrode. The theory is that contaminants transported in this way will be deposited at the electrodes which can then be removed and suitably disposed of or recycled.

World-wide, there are only a few case studies of using electrokinetics for remediation of contaminated land and no cases were found concerning in situ remediation of sediment, other that the trial for remediation of mercury contaminated canal sediments reported in full in Appendix 1. Unfortunately it was not possible to draw firm conclusions about the effectiveness of treatment. However the basis appears sound and the technology should be given more attention for research and development.

4.2.10 Ripening

Ripening of dredged material in a deposit is a natural drying process in which a slurry of dredged material is slowly transformed into a useful construction material. It is particularly suited to materials with a low sand content.

The material is put into a temporary deposit where dewatering and consolidation can take place. During and after dewatering oxygen is able to penetrate into the dredged material causing the oxidation of anaerobic organic matter and minerals. It is thought most likely to be applicable to treatment of PAH's.

4.3 Costs

The cost of treatment of contaminated dredged material has traditionally been perceived to be much higher than the cost of placement (PIANC 1996). In recent years the costs of treatment have decreased as new, more effective techniques have been developed. Also, many countries are experiencing severe shortage of placement sites and this has driven up the cost of placement.

The costs of the different treatment techniques can be accurately determined only in site specific terms. The factors to be included in estimating the costs were listed in Section 4.1.

It is extremely difficult to evaluate the costs associated with treatment technologies because the data are not collected in a uniform manner. Available data are inconsistent with respect to both the types of costs included and the units of measure. Geographical variations are not usually considered. Even if good costs data were to be available improved methods of measuring effectiveness would be needed for reliable comparative analyses of technologies on the basis of cost effectiveness. Post-project monitoring tends to be qualitative rather than quantitative.

4.3.1 US estimates

Although the cost data is limited it is sufficient for estimating cost ranges for various technologies. The costs of removing and transporting contaminated sediments (generally less than \$15-20/m^3) tend to be higher than the costs of conventional dredging (seldom more than \$5/m^3) but much lower than the costs of ex situ treatment (which can be well over \$100/m^3 and sometimes more than \$1000/m^3). For systems involving precision dredging or "near in-situ density" dredging there is potential for considerable cost savings especially if it reduces the need for pre-treatment dewatering.

When the volume of contaminated sediment exceeds about 10,000m^3, total treatment costs can be considerable but economy of scale reduces the unit cost.

Dewatering costs are in the range \$8 – 27/m^3 of slurry depending mainly on the solids content of the feed material (eg 10 – 40%)

Treatment costs can be reduced through pretreatment to separate contaminated silt and clay size particles from the generally cleaner sand. However, the cost of this process (\$23-54/m^3 for a volume of 10,000 – 100,000 m^3) is generally justified only if there is a large proportion of sand (eg >25%).

The costs of in situ treatment could be less than \$100/m^3 but in situ methods have had only limited success so far.

Given the chemical complexities of the sediment contaminant mixtures it is likely that in most cases a sequence of treatment processes will be required, as described for the case of The Netherlands below.

It is important to emphasise that the absence of detailed, reliable cost data does not pose a major barrier to project planning because the unique conditions (geographical etc) of each situation demand that costs always be estimated individually for each case. However improved reporting of cost information for full scale treatment systems would permit fair, overall comparisons and would provide benchmarks for future research and development and system design.

The National Research Council of the USA give the following order of magnitude costs for various approaches:

Table 4.2 NRC estimates of costs for various technologies

Approach	**Cost $/m^3$**
In situ natural recovery	<1
In situ capping	1
In situ treatment	10
Sediment removal and transport	10
Physical treatment	100
Chemical treatment	100
Thermal treatment	1000
Biological	100
Containment (CDF)	10

The question of cost versus effectiveness is one which every project manager will face. In particular, it is critical to not pay more for treatment than is necessary for the level of treatment required. For example, if it is intended to use the treated material as fill material for an industrial site there is no need to apply a technology that will treat the material to residential standards.

4.3.2 Canadian estimates for PAH's

Fig 4.1 shows a relationship between cost and treatment efficiency for PAH's as developed by the Great Lakes Clean-up Fund (Wardlaw et al, 1995, reproduced in PIANC 1996).

4.3.3 Dutch estimates for sandwinning

Gadella and Honders (1997) have produced a model which compares the costs of separation treatment in order to win sand with the cost of disposal. The model is based on the following input data:

- Quantity of annually dredged sediments divided into four classes by particle size distribution;
- The physical composition of the four classes;
- Costs for wet disposal;
- Costs for sandwinning.

The results of the modelling showed that sandwinning is an environmental and economically attractive alternative to disposal. The costs for sandwinning are in the same ballpark as the costs for disposal at relatively low disposal costs (20 – 40 Dfl/ m^3 ex situ). Therefore a large saving on both disposal volume and primary sand sources seems achievable. This appears to be true for any material containing more than 35% sand.

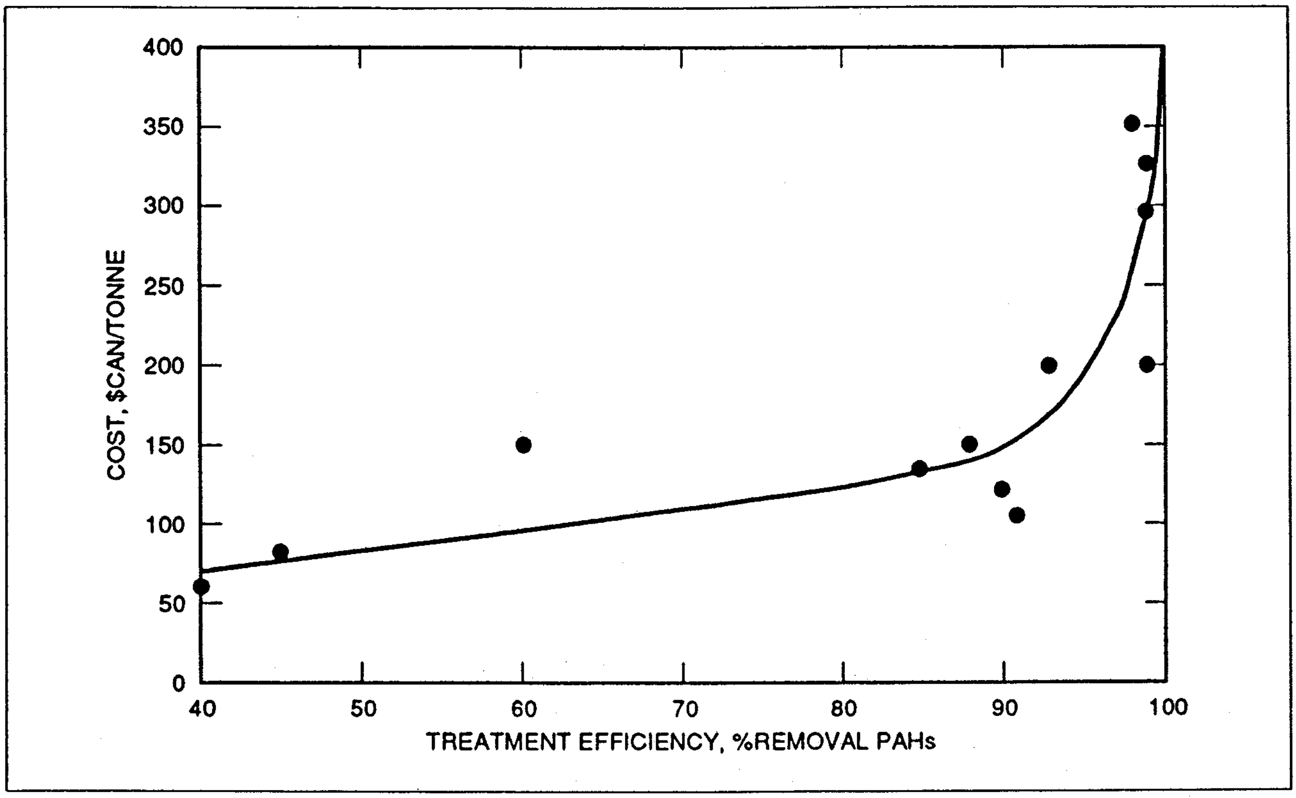


Figure 4.1 **Cost effectiveness of treatment of PAHs**

4.3.4 Belgian estimates for pre-treatment

Cost breakdown for dredging, physical processing and disposal

Dredging	BF 280/tonne	3-8%
Hydrocycloning and or dewatering	BF 2000 – 4200/tonne	50%
Dumping + environmental levy	BF 1450 – 4300/tonne	45%
Total	BF 3730 – 8780/tonne	100%

At the present time dredged material is classified as a special waste in many countries including Belgium and the UK. Nevertheless some environmental tax is levied in some cases.

4.3.5 Dutch estimates for remediation chains

Roeters and Bruggeman (1996) give estimated costs for a number of remediation chains, recognising that a single process is rarely sufficient to achieve full remediation.

Table 4.3 Remediation chains

A	Ripening
B	Landfarming
C1	Classification, polishing, dewatering of fine fraction, deposition of fine fraction
C2	Classification, polishing, dewatering of fine fraction, immobilising dewatered fine fraction.
D	Dewatering, immobilising
E	Classification, thermal treatment of sand fraction, dewatering fine fraction, depositing fine fraction
F	Depositing in large scale depots

Table 4.4 Estimated costs of remediation chains (NLG)

A	40	35-70
B	75	50-100
C1	80	70-115
C2	250	200-300
D	500	350-700
E	135	115-150
F	30	25-45

Note: costs exclude dredging and transport costs and VAT but include costs of disposal of residues.

4.3.6 Dutch estimates for a range of bioremediation technologies

Biodegradation techniques are compared by Ferdinandy (1996 and 1997). Assuming that the environmental assessment of the techniques will not result in significant differences and that the required product quality can be reached the choice between techniques depends on the available money, time and space.

Table 4.5 Bioremediation technologies compared

Technology	Suited for	Residence time	Space m^2/tonne	Space to treat 50,000 t/year	Energy Kwt/tonne	Costs Dfl/tonne
Greenhouse farming	Sandy CDM 60% dry matter	1-3 months	1.27	8000 – 20,000	6 – 18	23 – 33
Intensive landfarming	Sandy CDM 45% dry matter	1-3 years	1.7	150,000 – 200,000	0.6 – 1.0	44 – 62
SDP	All types CDM 30% dry matter	8-12 days	2.5	900 – 1,400	30 – 48	60 – 68
CBC	Fines only 20% dry matter	8-16 days	4.0	1,500 - 3000	30 - 52	66 – 76

4.3.7 Summary

The above published information gives some indication of the range of costs for various types of treatment in different countries. The general conclusions seem to be consistent that pre-treatment is the cheapest applied technology. Biological processes are next cheapest but only deal with organics. Other forms of treatment are very case specific and very expensive.

5. CONCLUSIONS

A wide variety of treatment techniques are available for contaminated dredged material. The currently available techniques can destroy, remove or immobilise a wide range of contaminants and are applicable to almost all types of dredged material. The costs are still high but are decreasing.

Full-scale separation and dewatering techniques are already being used internationally to good effect. Flotation and gravitational separation are very promising, lower cost techniques that have been used successfully at a number of sites. In particular one plant installed in Hamburg, Germany is processing close on 1 million tonnes/year of sediment in this way and is recycling much of the processed material.

Thermal treatment technologies have been used at a number of very highly contaminated sites in North America with success but at high cost.

Biological remediation appears to offer the most cost-effective treatment for organic contaminants. Landfarming and bioslurry treatment are likely to be the most cost effective but it may prove difficult to achieve target residual levels. The targets should be reviewed in the light of what is reasonably achievable, and what genuinely constitutes a threat to the environment.

Of the in-situ technologies electrokinetics appears to offer good prospects but is poorly researched so far.

Each dredging problem involving contaminated material is a unique situation that demands a custom tailored solution. For each site, the optimal combination of treatment technology must be determined by weighing technical, economic, social and environmental factors.

As placement costs continue to rise due to shortage of landfill sites and due to various forms of environmental taxation the treatment of contaminated dredged material will become more attractive.

By commercial necessity, ports are located in quiescent waters, which are also natural sediment traps. Because accumulations of sediment interfere with deep-draft navigation ports need to dredge periodically. If the sediments to be dredged are contaminated then ports are responsible for what happens to that sediment and any necessary remediation. The present situation is that most contaminated dredged material in the developed countries is dealt with by placing it in confined disposal sites either on land or in subaqueous pits. In many developing countries any special handling is regarded as an unaffordable luxury and marine disposal continues in contravention of international conventions and guidelines.

In most countries the availability of such disposal sites is not likely to meet future demands. Furthermore, pressure will be put on this approach by a public which views burying contaminants as a "time bomb". Inevitably the lack of disposal site capacity has to be offset by the full-scale use of options such as treatments and beneficial uses of dredged material. These should become the predominant choices for future dredging operations.

Furthermore the contaminated materials in many existing disposal facilities will have to be reclaimed in order to restore capacity and to meet public demand.

There is thus a demand for cost-effective treatment on a large scale. At present the ports face an unfair share of the responsibility for the remediation and placement of contaminated sediments. Perhaps the responsibility should be shared nationally. Various international and national policies incorporate the "polluter pays" principle. However, faced with diverse contaminants from numerous sources, both historic and present day, it seems like an impractical, tedious and costly if not impossible scenario in most cases. Upstream generators of contaminants often cannot be identified or held accountable, leaving ports to manage the problem. Historically some actions have been ignorant of the consequences of a careless attitude to waste disposal. It has wrongly been assumed that the assimilative capacity of the aquatic environment was infinite. It seems reasonable that the costs of cleaning up historic contamination should be shared.

The only long-term and cost-effective solution has to be control of pollution at source. In the meantime governments and industry should work together to develop technologies capable of cleaning up the mess. Taxes on existing polluters is one way of generating funds for research and development. In the USA the "Superfund" has financed several demonstration projects. In the UK the "landfill tax" was also intended to generate funds. However, the uptake so far has been small and rules governing research grants lack flexibility, requiring, for example, that the researcher has to based at a site within a certain distance of a landfill site.

Actually, the size of the problem of contaminated sediments in the UK is relatively small. However, taking a view of Europe, particularly Eastern Europe with its many heavily polluted inland waterways, there would appear to be a significant market for cost-effective technologies. There is no doubt that UK organisations have the necessary skills to carry out the development but, other than for primary separation and dewatering treatment, the financial risk of development is high. There is a strong case for government investment in technology development.

The results of the bench scale, pilot scale and occasional full scale trials investigated in the context of this research project give sufficiently positive indications to justify further research and development initiative in the UK.

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Appendices

Appendix 1

Project report - Use of electro kinetic treatment to remove mercury from a canal in Scotland – field trial. (CIRIA Report).

Trial Report Ref RP 489-11

In-situ electrokinetic remediation of mercury contaminated canal silt

Prepared under contract to CIRIA by

HR Wallingford

Executive summary

1. CIRIA has established a framework protocol for reporting the demonstration of land remediation technologies. One of the aims of the programme was to provide state-of-the-art reviews and guidance documents. HR Wallingford were commissioned by CIRIA to observe and report on a trial involving *in-situ* electrokinetic treatment of mercury-contaminated canal sediments.

2. The canal requiring remediation was under the authority of British Waterways (BW). British Waterways, with the aid of Millennium funding, are to forge a link between Glasgow and Edinburgh, a connection broken over sixty years ago, by opening and connecting the Union Canal with the Forth and Clyde Canal.

3. In one region of the Union Canal, the canal sediment is contaminated. A solution needs to be determined whereby the sediment is dredged and disposed of or cleaned up before the link is made. The sediments along the 9-km stretch are highly contaminated with mercury (both inorganic and methylmercury) thus jeopardising the canal water quality, particularly when the sediments are disturbed and re-suspended by boating activities.

4. Contamination of the canal sediments has occurred as a result of the historic use of mercury by a local ammunitions factory. British Waterways commissioned a contractor to run a remediation trial along a 60-m stretch of the Union Canal. The role of HR Wallingford Ltd was to observe, report, and make recommendations on the trial of an *in-situ* treatment of mercury-contaminated canal sediments by means of electrokinetic remediation. Electrokinetic treatment involves the separation and removal of mercury from the canal sediments by applying a direct electric current to the sediment via electrodes placed into the sediment.

5. The overall aim of the trial was to treat a 60 m stretch of the canal and remove mercury contamination so that average concentrations in the sediments would be below 15mg/kg (dry weight). Previous surveys by BW indicate contamination of mercury in the canal sediments of up to 12,100mg/kg (dry weight).

6. At the initiation of the trial, it was agreed that it should be run in two phases with approximately 20 m of canal sediments to be treated in Phase 1 and a further 40 m in Phase 2. About 16 m of Phase 1 of the trial was completed and is reported here, but there is no evidence to conclude that it was effective. At the time of writing, Phase 2 is under consideration.

7. There remain design and operational difficulties, e.g. in the design and placement of electrodes, which would have to be resolved before full-scale electrokinetic treatment could be considered.

8. General lessons from the trial include the importance of setting up consistent sampling methods and rigorous and tested analytical procedures before beginning treatment and of clear communications.

1 Introduction

British Waterways (BW) wish to re-establish a waterway link between Glasgow and Edinburgh, Scotland, that was broken over sixty years ago. The link is for recreational purposes and it is to be made by opening and connecting the Union Canal with the Forth and Clyde Canal. Past industrial activity has resulted in parts of the Union Canal being contaminated with mercury, which will have to be remediated before the canal opens again. BW, therefore, sought to investigate the *in-situ* canal sediment treatment method of electrokinetics.

In the summer of 1997, BW commissioned a contractor to carry out an *in-situ* remediation trial along a 60-m stretch of the Union Canal. HR Wallingford were commissioned by the Construction Industry Research and Information Association (CIRIA) to observe, report and make recommendations as necessary on the trial. The reporting would be in accordance with CIRIA *Framework Protocol for Reporting the Demonstration of Land Remediation Technologies* (CIRIA, 1996).

The contractor's commission from British Waterways (BW) was to run the electrokinetic remediation trial on a 60-m stretch of the Union Canal sediments to reduce mercury concentrations to below a specified concentration. The trial was to be run in two phases.

Phase 1 of the demonstration trial was to involve the placement of electrodes and treatment of a 20-m plot for approximately 3 weeks (Plot 1). Phase 2 was to continue to treat Plot 1, if necessary, and to treat a further 40-m plot. A length of about 16 m has been completed under Phase 1 and is described in this report. Phase 2 remains under consideration.

1.1 BACKGROUND

BW have identified their need to remediate approximately 9 km of the Union Canal before the canal is joined with the Forth and Clyde Canal. Site investigations showed high concentrations of mercury in both the canal sediment and in parts of the surrounding land. The source of the mercury is likely to have been a local ammunitions factory, which ceased to operate in the 1950s. The canal sediments along this stretch of the Union Canal are reported to be contaminated with both inorganic (elemental) and organic (methylated) mercury (Dames and Moore, 1995). It is possible that land run-off introduced inorganic mercury into the canal sediment and microbial activity, over the years, has transformed some of that mercury into methylated mercury. Another pathway of mercury into the canal could be from atmospheric fall-out. This form of mercury is highly toxic and can be transferred up the food chain easily, with serious human health and ecological implications.

Recreation activities, such as boating, stir up canal sediment, which would result in the re-introduction of both forms of mercury into the canal water reducing water quality. BW have been investigating a number of canal sediment remediation methods, both *in situ* and *ex situ*, to reduce mercury concentrations in the sediments so that the Environmental Quality Standard for the canal water would not be breached on re-introduction of recreational activities. At the time of writing, landfill is an option for disposal of the contaminated sediments. When the study was initiated the landfill disposal option appeared not to be feasible because of the high mercury concentrations in the sediment, so BW decided to investigate the feasibility of the electrokinetic method to reduce the mercury contamination. An advantage of an *in-situ* method is that it is potentially less intrusive and physically damaging to the canal system compared with the conventional method of dredging the sediments followed by disposal. Many details of the *in-situ* electrokinetic method for this remediation, however, have not been made available by the contractor for reasons of commercial confidentiality.

The contractor commissioned to run the *in-situ* trial using electrokinetics along a 60-m stretch of the Union Canal, was given and accepted a targeted sediment level of mercury after remediation of 15 mg/kg (dry weight). BW and the contractor agreed to run the trial in two phases. Phase 1 would cover the first 20 m of the identified trial stretch, and Phase 2 the remaining 40 m.

Staff from HR Wallingford participated in the meetings between BW and the contractor as observers to the trial. Where appropriate and with the agreement of BW, HR Wallingford made recommendations for the trial set-up, the sampling and analysis specifications, and the health and safety and planning aspects. A member of HR Wallingford staff was also present at some of the sampling events as an observer only.

As only Phase 1 took place, this report covers the planning stage of the trial, the trial run, its findings and recommendations.

1.2 REPORT STRUCTURE

The scope of this report is largely a record of actions and obeservations of what was a small-scale trial. Contractual and operational difficulties limited what could be learnt. The report contains background information on the contractual arrangements, aims, and setting of the trial. The technology and its application are described in Section 2. Sections 3 and 4 describe the preparation stage and the trial, respectively. The information gathered is presented in Section 5 with a discussion of its reliability and limitations in order to assess the effectiveness of the trial. Some of the wider environmental and health implications are introduced in Section 6 such as the effects of the treatment on local water and air quality and on the aquatic life. Section 7 assesses some aspects of the feasibility of the full-scale application, while the broad costs of the trial are summarised in Section 8. The report draws conclusions from the trial, recognising that many uncertainties remain and makes recommendations for any subsequent trials.

1.3 CONTRACTUAL ARRANGEMENTS

The administration of the trial, the identity, roles and responsibilities of the various trial participants and how they relate to the demonstration are listed in Table 1.
HR Wallingford was contracted to CIRIA to report on and draw out guidance from the trial.

Table 1 *Participants: the roles and responsibilities of the demonstration trial*

Participant and role	Responsibilities
British Waterways- site owner who contracted the trial	To specify requirements for the trial
Contractor- main contractor who has the rights to the specialist remediation technology under trial	To carry out the trial according to a specification and with adequate Health and Safety precautions
HR Wallingford Ltd- independent observer and research contractor to CIRIA	To observe the progress and outcome of the trial, to report the trial findings in a document in accordance with CIRIA Framework Protocol

CIRIA- indirect observer through contract with HR Wallingford under their CIRIA Framework Protocol	To liase with HR Wallingford on the monitoring and reporting of the trial, to publish research
Scottish Environmental Protection Agency (SEPA)- regulatory authority responsible for the water quality	To monitor the water quality during the demonstration trial

1.4 AIMS OF THE DEMONSTRATION TRIAL AND REPORTING

The overall aims and objectives of the observations of the trial were as follows:

1. To set up suitable criteria by which to assess the effectiveness of the trial.
2. To evaluate the technical performance of *in-situ* electrokinetic treatment specifically for the removal of mercury in contaminated canal sediments.
3. To attempt to answer by the trial the following questions:
    - how effective is the technique?
    - how effective is it for the removal of mercury?
4. To evaluate operational and other practical requirements.
5. To highlight environmental implications of the trial.
6. To collect information on costs.
7. To assess regulatory acceptance and authorisation procedures and timescales.
8. To determine the applicability of the electrokinetic method for the full-scale treatment of 9 km of the Union Canal sediments.

This report comprises a description of the observations listed above and the findings.

1.5 GENERAL DESCRIPTION OF THE FIELD TRIAL

The Phase 1 trial consisted of the following steps:

- selection of the trial site, which was undertaken by BW and the contractor
- installation of power supply
- installation of remediation equipment
- operation of remediation equipment
- sampling and monitoring of canal sediments and water before and during the remediation
- removal of contaminated electrodes for disposal or extraction of the mercury.

The trial was to be undertaken without lowering the canal water. The Union Canal is a contour canal and there are no locks in its 50-km length. Lowering the water level would require either draining the whole canal or installing cofferdams at each end of the section. The latter would need pumps to keep the water level down and a by-pass to maintain levels and flow within the remainder of the canal. For a trial, the cost of placing and removing the cofferdams would be prohibitive, but they should remain as an option to be used for dealing with a long section of heavily contaminated silts. Any works also have to take account of the canal being a scheduled ancient monument, with due care given to the canal structure along the trial stretch.

A health and safety assessment was undertaken by British Waterways and a health and safety plan drawn up with the contractor providing a method statement and risk assessment. This was undertaken as a precaution as it was not clear whether this project would fall under CDM or not, but as it was a borderline case, British Waterways insisted it was treated as such. The relevant documents received to date are given in Appendix A1. At the start of the trial it was agreed that the risk assessment would be reviewed by the above parties every two weeks. A final report describing the results of the trial was submitted by the contractor to BW (Appendix A5).

9 Conclusions and recommendations

9.1 CONCLUSIONS

Based on site observations and the results of laboratory analyses, the following conclusions are drawn:

1. There is no evidence to conclude from the trial that it was an effective method for remediation of mercury in the canal sediment.

2. Demonstration objectives were not all met. The trial was set up but there were several delays and the trial plan and timetable was continually changing. In addition, changes frequently were not well communicated.

3. The aim of the remediation trial was to reduce mercury concentrations in the sediments by several orders of magnitude. The target was to reduce mercury concentrations in the sediments to below 15 mg/kg. From the evidence of the sediment data supplied, the concentration of mercury did not appear to have been reduced, but remained at the same order of magnitude.

4. Various explanations have been put forward for the fish kills known to have occurred on two occasions, but detailed investigation was not made.

5. The access to power and a constant and reliable supply of energy to the electrodes is of great significance to the effectiveness of this technology.

6. The type and design of electrode influences the effectiveness of this technology.

7. Access to the canal for placement of the electrodes was good for the trial. It is recognised that this will not be the case for the whole 9 km stretch of the canal requiring remediation.

Interpretation for the trial sediment data was not possible because of the poor quality of information supplied and the wide variability in ten results, as explained in Section 5. Although it has not been possible to evaluate the trial, four scenarios can still be considered as possible:

1. The data are not sufficient or reliable enough to draw conclusions about the effectiveness of the trial as a whole, but evidence of changes in mercury concentrations with depth perhaps indicates that electrokinetics can mobilise mercury in the canal sediments.

2. The electrokinetic treatment does remove mercury from the sediment, but that where concentrations appeared to increase it was the result of recontamination events following intensive rainfall.

3. The electrokinetic treatment mobilises mercury within the sediments relocating it to other zones of the sediment.

4. The electrokinetic treatment removes mercury from parts of the sediment but it also results in other chemical changes in the sediment and water with significant consequences for the aquatic biota.

In order to ascertain if one or more of these scenarios actually took place, a comprehensive sediment and water quality survey would be needed. Appropriate recommendations are put forward in Section 9.2 below.

9.2 RECOMMENDATIONS

1. Soil and sediment types vary considerably in their concentrations of contaminants as well as constituents such as organic and inorganic material. Laboratory studies should therefore be carried out to assess whether electrokinetic treatment is suitable for a particular contaminant and soil or sediment type.

2. The methods of sampling and analysis of sediment samples needs to be evaluated and standardised in order to measure the degree of success of the procedure.

3. A drying and crushing technique used for sample preparation was investigated by the laboratory and shown to give better homogenisation. This method is recommended for future work if the deposits are old with little likelihood of volatile mercury compounds.

4. It has been suggested by the contractor that the canal is being continually recontaminated from the source site and that demonstrating remediation of the sediments may not therefore be possible. The likelihood of recontamination needs to be investigated and established before a full-scale project.

5. The placement of the electrodes proved to be much more difficult and time consuming then expected. Alternative electrode designs instead of the steel pipes were therefore considered. Alternative electrodes such as steel plates may need to be built into the full-scale project contingency.

6. The measurement of volatile organomercury compounds is relevant to the assessment of air quality with possible health implications for site staff and residents. It is recommended that a comprehensive sediment survey is carried out to establish the amounts of volatile compounds.

7. The fish deaths recorded on two occasions highlighted the possible biota implications of placing electrodes in the canal and applying a direct current. It is recommended that such environmental implications are investigated, prior to another trial or the full-scale treatment.

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Appendix 2

Project report – Hamburg

Appendix 2 Project report – Hamburg

In the course of these investigations two visits were made to Hamburg to inspect the MEHTA plant operation. The Port Authority gave full co-operation and detailed information was provided and is presented in this appendix.

Every year Hamburg produces on average about 2 million m^3 dredged material in the course of maintenance dredging, a large proportion of which is regarded as contaminated. The following table illustrates the degree of contamination measured since the 1980's although more recent measurements show a considerable reduction.

Table A2.1 Concentrations of various contaminants in Elbe dredged sediment

Parameter	Concentration mg/kg
Arsenic	50-150
Lead	150-300
Cadmium	5-25
Chromium	150-300
Copper	250-600
Nickel	50-100
Mercury	5-20
Zinc	1000-2500
Mineral oil	up to 3000
Sum PCB (6)	up to 1.5
Sum PAH (6)	up to 15
Dioxin	100-200 ng TE/kg
Sediment size	50-98%<0.063mm
Organic content	12-36%

In the mid 1980's the "longitudinal classifier" was introduced. These are long fields with a small gradient where the dredged slurry is piped in at the higher end. When flowing through the field the sand settles and the silt is collected in a large basin. The water is drawn off. The dry sand is taken out with conventional plant and the silt is re-dredged and pumped to dewatering fields.

These fields are about 2-3 ha in size and sealed with a layer of specially selected silt and a synthetic liner at the inflow point. After one year of exposure to sun and wind the silt is sufficiently dewatered and can be taken out to be deposited.

This processing requires large areas and is also very dependent on the climate. To overcome these problems the MEHTA plant was developed. This performs the same steps but in a completely mechanical way.

To build such a facility, research had to be undertaken on a laboratory and pilot scale. In 1987 the pilot plant came on line to help to optimise the process. In 1990 it was decided to build a large scale MEHTA plant. Construction was completed within two years and the plant was inaugurated in 1993. A diagram of the installation is shown in Fig A2.1

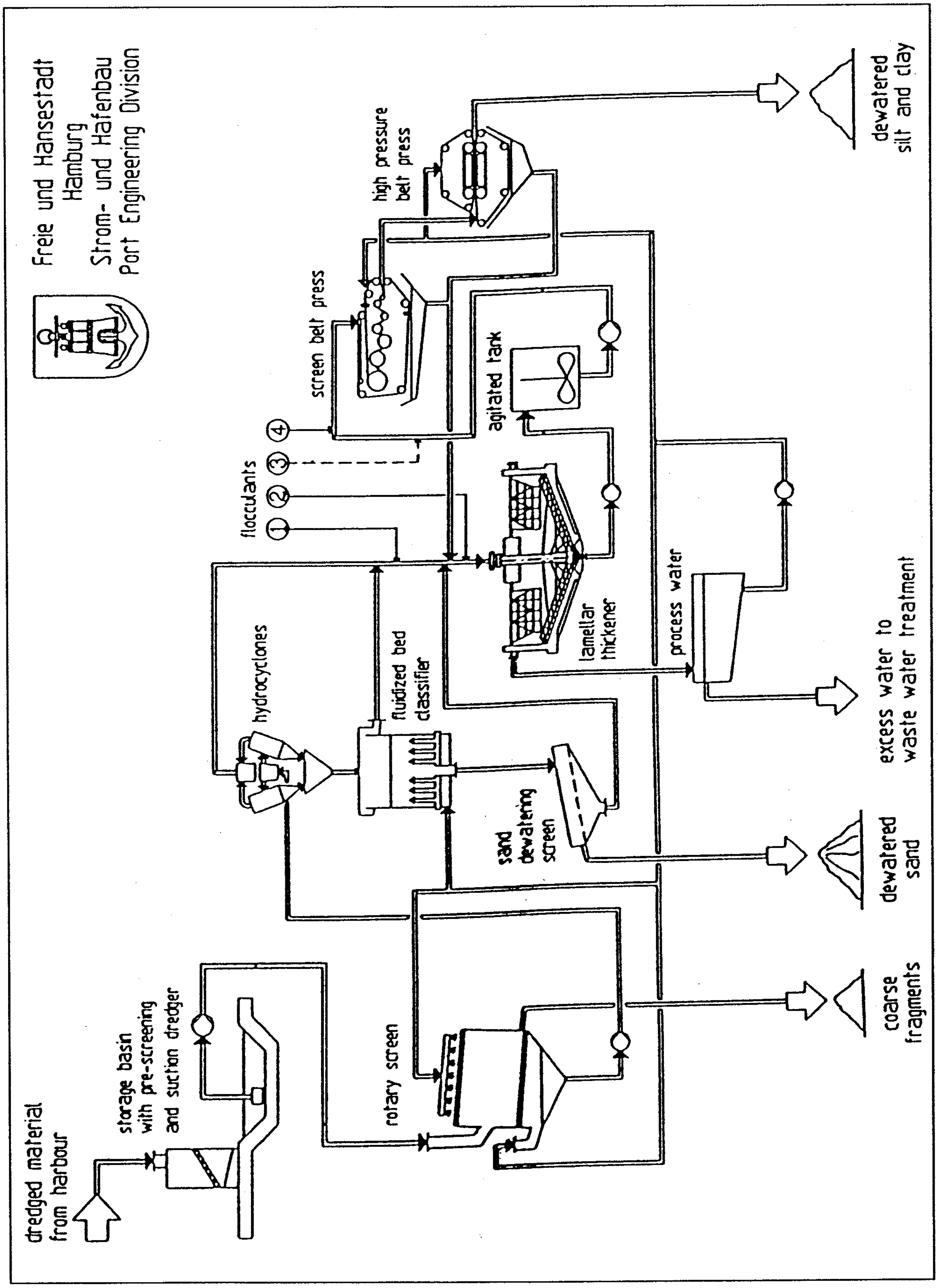

Figure A2.1 Figure of the installation

The dredged sediment is supplied from the dredgers by means of barges, taken up by barge suction dredgers, pumped out and first stored temporarily in a large basin. Before flowing into this basin the coarse impurities are separated out. In a second separation process, at the start of the processing method, all particles larger than 10 mm are sieved out using a drum filter. The fine material remaining is mixed thoroughly in a homogenisation tank and then pumped into the two-stage separation plant, comprising hydroclassification and up-current sorting.

The heavy metals and organic contaminant contents are primarily governed by the grain size distribution of the sediments. The finer the particles and the higher the content of organic matter in the sediment, the higher the contaminant content. Thus, for a reliable handling of the dredge material, the first stage of treatment has to be the separation into the silt and sand fractions.

In the first separation stage, hydroclassification, most of the finest particles are separated from the sand by very high centrifugal forces. The bottom flow from the hydrocyclones, the sand with residual finest particles, is then fed to the second separation stage, the sorting unit. Here, the remaining (lightest) fine particles are flushed into a fluid bed by adding up-current water which the sorter pumps from the bottom to the top and, together with the finest particles from the hydroclassification, they are transported further for concentration.

The clean sand removed from the sorting procedure is passed through a dewatering sieve where it is dewatered to about 85% dry content and removed from the plant via conveyors for further use.

The fine silt suspension from the hydrocyclone and upcurrent sorter overflow, which contains a very large proportion of water, due to the efficient separation process, is first concentrated in purifiers by adding flocculents to increase the solid matter content. The purified overflow concentrate is re-used as process water.

The silt is then pumped to six dewatering lines. To dewater the silt, polyelectrolytes are again added at this stage. This results in the formation of more compact silt floccules that are easier to dewater. A dewatering line comprises a sieve-belt press and a high-pressure post-dewatering press. The suspension is transported between endless circulating filter cloths. The ever-increasing pressure forces the water out of the compressed cake. The dewatering process has a total capacity of 60t dry matter per hour.

Whereas the sieve belt press dewaters the silt to 48% dry content, the high-pressure post-dewatering process increases this to approximately 55%. The objective of this dewatering is to obtain an end product with sufficient shear strength ($c_u > 20kN/m^2$) from a mechanical aspect. The total flocculent used varies between approximately 1000 and 1900 ppm, depending on the solid matter content.

To enable the various sections of the plant to operate at optimum efficiency at all times and to adapt to the changing conditions (i.e. properties of the dredged material), the plant contains a large number of measuring transducers and a process control system.

The dewatered silt is transported out of the plant with conveyor belts to the mound building site. The excess water from all the processes in the MEHTA system is fed to the wastewater treatment plant. The throughput of the solids fraction amounts to 600,000 tonnes/year, corresponding to 1.2 – 1.4 million m^3 (in situ) with 50% of the solid having a grain size of <0.063 mm. The production of sand and silt is therefore in the region of 300,000 tonnes/year each.

The plant is operated five days/week with a staff of 100, with a 24-hour operation of the dewatering section. Investment expenditure amounted to \$80 million; the operating costs are in the region of \$8 million, which equates to a rate of about \$6/m^3 (in situ vol.).

The port does not see this as a long-term solution. They emphasise that the pollution must be controlled at source.

Appendix 3

Project report – Blyth

Appendix 3 Project report – Blyth

The following is a personal account provided by Colin Robson of Northumberland County Council of the difficulties he experienced in dealing with the real problem of PCB contamination at the Port of Blyth. It is presented verbatim deliberately to allow the sense of some of the frustrations to be communicated. There are lessons to be learned at all levels from this experience.

Appendix 3 Project report- Battleship Wharf Scheme, North Blyth

Colin Robson, Northumberland County Council

REMEDIATION OF CONTAMINATED RIVER SILTS

DON'T PANIC!

The problem of Contaminated Land in Britain is a serious one, however, the title of this presentation is, I think, appropriately called Don't Panic.

When I became involved with the Battleship Wharf Scheme in Northumberland there was great clamour from the Press, the Public and most of all the various Regulatory Bodies over the problems associated with the site.

There certainly were plenty of problems, after 85 years of shipbreaking the site was contaminated with 60,000 cubic metres of asbestos laden soils, heavy metals including lead, mercury and cadmium and worst of all transformer oils containing PCB's. The latter had been discharged onto the site and into the adjacent tidal dock and river from dismantled Soviet Warships.

Having worked for 25 years on contaminated land sites, mostly on former colliery areas, I was fully aware of the regulatory framework within which I would have to operate.

Less expected was the initially negative approach taken by NRA and MAFF especially in response to the PCB problem.

Something I am pleased to say was quickly overcome.

The site is in the control of the Port of Blyth which is administered by a Board of Commissioners and a Chief Executive. When, following the discharge of oils, the Port were asked to deal with the problem they searched for a firm who could handle PCB's. A previous speaker at this symposium is an employee of a company who showed some knowledge of the problem and you have heard his approach. On my part, at that time, and still, I am not convinced that a cost effect treatment exists for this problem.

To understand what his company and later others were suggesting to me it was necessary to carry out a detailed trawl of the published literature on PCBs. This was done and has produced by purchase, borrowing and photocopying what is I guess one of the most comprehensive libraries on the topic available. That part was easy, reading it all, understanding it and trying to reconcile conflicting evidence and views was another matter.

One of the first lessons was that measurements of levels of PCBs, depending on the protocol used, could vary widely. Further, some of the levels of reduction required by MAFF were at the limits of detection technology.

The basic practical problem was that the MAFF would not issue a licence to tip dredged material at sea that contained PCBs at levels above 200 parts per billion. Such a licence is obviously vital to keep the Port operational. A chart of surveyed samples showed a contour of material above this level lying off the tidal dock, with a maximum of 50 parts per million in the dock. There was one plus factor here in that the River Blyth is a low energy system and silts do not move very far during the rise and fall of tides.

Following the initial stage of understanding the material we were dealing with , several things were evident and had to be agreed with the regulators:-

- The PCBs above the 200 parts per billion contour had to be brought ashore and treated.
- An environmentally safe method of dredging was necessary.
- A decision had to be taken regarding encapsulation or treatment.
- The sampling work had to be extended and refined.

At this point it was already obvious that there would have to be some encapsulation of contaminants on site. The site investigation had shown that the old quay was contaminated with a mix in the soil of asbestos, oils, heavy materials and PCBs. This mix meant that even if the technology for remediation was available, it would be very expensive. None of the contaminant levels on site could be classified as extremely high.

There is therefore still a solution to the problems of the dredged silts of including them in the stabilisation and encapsulation process.

The encapsulation was then considered and it was decide to construct a retaining bund across the old tidal dock behind which the contaminants could be encapsulated. This was later refined into a new quay wall with additional funds from the Port of Blyth.

At this construction was to be across open water it was decided to use a system of 13 metre diameter circular steel cells which required a level river bed as a formation. This design meant a sophisticated environmental and engineering dredging contract to first remove the contaminated silts and then allow clean silts and rock to be dredged and tipped to sea. This contract was prepared and put out to tender.

When the tenders were returned they were some £300,000 over estimate and the scheme was in jeopardy. The dredger however could never reach into the tidal dock so this was cleared by machine and dump trucks at low tide. A piece of good fortune at this time was exceptionally low tides which allowed clearance beyond the end of the tidal dock.

Simultaneously more refined results from sampling carried out by the NRA showed that 95% of total contamination was within the area that had been cleared. This threw into even greater relief the extra cost of "environmental dredging".

In discussion with the Port of Blyth's Engineer he identified that he operated a river bed "plough" which could move the contaminated silts within reach of an extended reach excavator. It was estimated that this would reduce the remaining contamination to 1-2% of the original total.

Whilst the river silts contained the lowest amounts of PCBs, they were in a ratio of 4 to 1 by volume with the tidal dock extract. However in terms of their concentration of PCBs they were no worse than other materials found in industrial areas nationally, being in the range 0.2 to 1 part per million.

Both the NRA and MAFF agreed this procedure and over a three week period the contaminated silts were brought ashore and stored in a temporary lagoon.
It has been decided to dewater the river silts using a filter press system and the material will then be mixed with courser soils and used as general fill in non-developable areas of the site.

The jury is still out on the treatment of the tidal dock material. As I said earlier, I have yet to be convinced that a verifiable treatment for the reduction of PCBs to industrial background levels exists. In support of this I would sight a recent conference in Maastricht on contaminated land treatment which in out of 100 papers and 150 poster presentations hardly mentions PCBs at all.

At present my preferred option remains encapsulation although whilst awaiting the bund/dock walls construction, which will take 10 months, I remain open to offers.

Appendix 4

Project report – Manchester Ship Canal

Appendix 4 Project report – Manchester Ship Canal

In the course of the research HR Wallingford were asked to carry out an assessment of the quality of the sediments of the Manchester Ship Canal and consider the treatment options. This was carried out at the expense of the Manchester Ship Canal Company and the results are made available to the research as a contribution.

A.4.1 Background

The Manchester Ship Canal Company (MSCC) has an on-going commitment to maintenance dredging of the Manchester Ship Canal (MSC) in order to permit navigation and to facilitate drainage from a large area of North West England. Dredging is carried out on a continuous basis and on a yearly cycle the complete length of the canal bottom is dredged back to declared bed levels.

The bulk of the dredgings are natural silts and sands washed into the canal by the rivers Irwell, Mersey and Bollin (Fig. 1, taken from a report "Manchester Ship Canal: Upper Reaches - Part 1 Numerical Model Study" by Hydraulics Research Wallingford in 1986). The MSC was constructed in 1894 and before this time and if it were not present today, sediments would have been carried into the river Mersey and become part of the Mersey estuary regime.

Currently the MSCC collects and disposes of about 1 M m^3 of dredgings each year. The amounts of material dredged from each reach of the MSC are shown in Fig. 2 (ibid.). The material, which is deposited in purpose designed deposit grounds located adjacent to the canal, comprises about 20% of all UK maintenance dredgings disposed of to land.

The present situation is that existing MSCC deposit grounds, by sequential embankment raising, have sufficient capacity to receive dredged material for a long time. However, MSCC recognise the government's intention to minimise sacrificial disposal of waste material and are actively investigating alternative methods of disposal.

In order to establish the best practical and environmentally cost effective disposal, it is necessary to establish the physical and chemical characteristics of the dredged material. The sediments are known to be contaminated to a greater or lesser extent along the whole length of the canal as a result of industrial activities which are wholly outside of the control of the MSCC.

In December 1995 the MSCC commissioned HR Wallingford (HR) to undertake a preliminary feasibility study to evaluate options for the beneficial disposal of dredged material from the MSC.

A disposal framework involving an integrated assessment of disposal options will enable that the best environmental option can be determined to give an economically feasible solution. The first main step to such an assessment is adequate and sufficient characterisation of the dredged material and the site. Contaminated dredged material needs special attention and probably innovative solutions at an acceptable cost level compared against the current cost of disposal.

This report offers a discussion of the options and techniques available for the specific situation and site.

The contamination levels recorded in the sediments vary along the canal stretch with some sectors displaying background levels and others displaying the contaminants Hg, Pb and total PAH's at concentrations that are likely to compromise a number of placement options. Generally, the proportion of material that could be defined as more heavily contaminated depends on the standards employed but should probably be considered to be of the order of 50% of the total. Given this, assessing the potential role of treatment technologies as an integrated part of disposal options is warranted.

A4.2 Discussion of options

Physical

If contaminants are bound to the surface of particles the larger particles will have a lower concentration of contaminants per unit mass than the smaller particles. Therefore separating out the larger fraction would produce a fraction of the material with lower contaminant levels. This has proved to be an effective approach in Germany and the Netherlands.

There are three possible methods of separating sediments.

(i) Settlement in tanks or lagoons

The fine material remains suspended and is allowed to overflow. The degree of separation depends on the flow and trubulence through the settlement system and settlement tanks or lagons can be arranged in series so that coarse material settles in the first stage and progressively finer material in subsequent stages.

(ii) Sediment washing

Coarse material can be cleaned by vigorous washing with water, with or without chemical additives. Washing is not practicable for finer fractions since the suspended solids cannot easily be separated from the wash water.

(iii) Hydrocyclone

This is the most commonly used method for separating solids from liquid but it can only separate relatively coarse material (sand) and does not separate smaller particle sizes.
The use of a hydrocyclone involves costs, which can sometimes be recovered from the sale of sand recovered from the sediments. This is attractive when the sediments contain >60% sand, as they do in parts of Germany and the Netherlands, but the sediments from most sectors of the MSC contain only a very small proportion of sand and the hydrocyclone would not produce enough to make a useful contribution to its operational costs.

Crude estimates of total surface area suggest that some 50% of the larger particles would have to be separated and the cut off point would typically be less than 10 microns, which is very close to the operational limit and the capability of commercially available hydrocyclones.

Any form of mechanical treatment would result in a substantial increase in total disposal costs.

Physico-Chemical treatment

(i) Chemical extraction

The extractants can be acids, alkalis or chelating agents or other substances to detach contaminants from particles. If they are effective they all depend on being able to separate the solid material from the washings subsequently. For the fine sediments that typify those from the MSC this is at best likely to be both difficult and expensive.

(ii) Wet air oxidation

This involves treating sediments with oxygen at high pressures and high temperatures. It is effective with a large proportion of organic chemicals. It does not eliminate PCBs, however, although it is reportedly more effective in dealing with PAH's. The cost can be high.

(iii) Hydrothermal processing

Solids suspended in water are treated under very high temperatures and pressures sufficient to produce super-critical conditions. Under these conditions metals are converted to forms which separate them from the solid matrix. This too is a very expensive process and the fine particles must subsequently be separated from the water.

(iv) Base catalysed decomposition

This has been tried on an experimental scale for very heavily contaminated sediments dredged from New York/New Jersey Harbour. The method destroyed PCBs and chlorinated substances and is claimed to remove PAH's. It also removes mercury but not other metals.
It requires the separation of fine sediments from the reaction liquor, which, as stated before, would be likely to be costly and difficult for MSC sediments.

Biological

Biological processes in sediments can stabilise or mobilise metals, depending on conditions (eg methylation of mercury, conversion of lead to the insoluble sulphide), but cannot destroy them. Organic substances, on the other hand, can be converted by bacteria to more or less harmful substances or even oxidised completely to harmless by-products.

Biological treatment requires controlled conditions (water content, oxygen and nutrients are vital) and timescales of a year or more are often required for adequate reduction in contaminant concentrations to be achieved.

The lower levels of PAH's in samples from the old disposal ground may result from the gradual elimination of the very fine particles to which the PAH's may have been adsorbed but it may also be due in part to the biodegradation of the PAH's.

Treatment of PAH contaminated sediments with in-situ or commercially available bacteria capable of degrading PAH's is reported in the literature. However, currently there is some debate regarding the effectiveness of such methods especially the effectiveness of spiking sediments with bacteria populations which are not indigenous to the sediment. In addition, the final residual concentrations of PAH after treatment are of interest and may still be relatively high such that many disposal options are still restricted. A pilot scale evaluation using dredged material from MSC would be required if this route was to be investigated as an option in the future.

<u>Thermal Incineration</u>

Incineration would remove most organics but conditions have to be carefully controlled to remove PCBs. It volatilises mercury, which must be extracted from the flue gases before release to the atmosphere but does not remove other metals. The ash from MSC dredgings would still be highly contaminated and would require disposal at a licensed site. At higher temperatures the metal salts melt to form a slag in which they are effectively immobilised. Incineration is, however, so expensive that it could not be contemplated for the MSC.

Beneficial Use Options

There are a number of beneficial use options for dredged material, including the contaminated fraction, and these have been well documented in the 1992 PIANC publication on beneficial uses of dredged material (PIANC working group No 19). Since the PIANC publication, there have been a number of case studies, all of which focus on considering the dredged material as a resource. In some cases where the contamination levels were the prohibiting factor, decontamination was carried out prior to using the material beneficially.

The composition, chemical characteristics and grain size distribution of dredged material determine the beneficial use options available for dredged material. Uses to be considered include:

- Engineering potential
- Agricultural and aquaculture potential
- Aquaculture
- Construction material
- Environmental enhancement
- Restoration or creation of a wetland and a saltmarsh
- Upland habitats and bird nesting islands

Appendix 5

Project report – New York/ New Jersey

Appendix 5 Project report – New York/ New Jersey

In the course of HR Wallingford's investigations an opportunity was provided to make a visit to New York to discuss the problems of what to do with the contaminated sediments of the New York/New Jersey Harbour and inspect the immobilisation treatment which was in progress. Meetings were held with representatives of the Environment Protection Agency, US Department of the Environment, New York/New Jersey Port Authority and the Army Corps of Engineers New York office. A large amount of information was made available from which the following summary has been produced.

A5.1 Background

The maintenance of the Federal navigable shipping channels in the NY/NJ Harbour is the responsibility of the New York District of the U.S. Army Corp of Engineers (NYDCOE). Dredged material from the Harbour's navigable channels has historically been disposed of in a designated ocean dump site. The dredged material disposed of in this way may contain a variety of organic and inorganic contaminants. Recent regulatory changes have made the nations ocean dumping criteria more stringent and this has resulted in a potentially significant increase in the volume of dredged material prohibited from unrestricted ocean disposal and requiring instead more costly disposal options such as the use of containment islands, borrow pits, or land disposal in secured landfills. Responding to a potential crisis the U.S. Congress, under the Water Resources Development Act (WRDA) of 1990, directed the U.S. Army Corps of Engineers (Corps) and the U.S. Environmental Protection agency (USEPA) to address the sediment management problem and to identify potential solutions.

The U.S. Environmental Protection II (EPA) and the U.S. Army Corp of Engineers- New York District (COE-NYD) are actively seeking and investigating sediment decontamination technologies for dredged material management. Section 405 of the Water Resources and Development Act 1992 authorised an investigation, including testing and demonstration, of decontamination technologies and their potential application to contaminated sediments to maintain harbour navigation in an environmentally acceptable, cost effective manner. The evaluation of innovative and fast-track decontamination technologies (INV/FT Evaluation) appropriate for the treatment of the Harbour sediments was therefore undertaken.

New York/ New Jersey Harbour has presently restricted dredging due to the problem of disposal of the dredged material. Under the 1992 disposal of dredged material criteria, over 75% of the material in the Harbour, which would be collected from essential maintenance dredging, is contaminated to the extent that it can not go to ocean disposal. In addition, the MUD Dump Site was to be closed in September 1997. Since the sediments are contaminated, a solution to their disposal needed to be found. This resulted in a Congressional obligation to treat (i.e. remove or reduce) contaminant levels in the dredged material. A dredged material management plan (DMMP) was made.

From this on-going process a lot of lessons can be learnt and valuable information reviewed. The management and method of approach in assessing the problem and searching for disposal solutions is of direct interest to this project. It has previously been mentioned that treatment technologies can not be evaluated in isolation of the dredging and disposal solution. Therefore, there are a number of areas of direct interests to this project.

- Evaluation of the problem
- Selection process of potential decontamination technologies
- Decontamination technologies
- Pilot studies
- Conclusions and recommendations

A.5.2 Evaluation of the problem

Treatment will likely require several different procedures before disposal is possible due to the complex and varying nature and levels of the contaminants and their widespread spatial distribution within the Harbour. A solution is therefore expected to involve the integration of a number of steps (e.g. dredging, transportation, pre-treatment, treatment, post-treatment and disposal or resuse) into a system which can be used on a regular basis. Although the exact amount of material requiring treatment in the future has yet to be determined, an estimate of approximately 500,000 cubic yards (cy)/ year is the target figure for protecting full-scale operations.

Dredged sediments form various areas of the harbour contain elevated levels of one or more of the following contaminants: heavy metals, polynuclear aromatic hydrocarbons (PAH's), and organochlorines such as dioxins, furans, polychlorinated biphenyls (PCBs), chlorinated pesticides and herbicides. Technologies which remove or detoxify only one contaminant or contaminant class will be considered; however, preference will be awarded to vendors whose systems are capable of successfully treating multiple contaminants. Treatment systems must be capable of sufficiently reducing the contaminant levels by separation, destruction, immobilisation or other methods that render dredged sediments suitable for unrestricted ocean disposal, or preferably, beneficial use.

A.5.3 The port and trade

The Port of New York and New Jersey stands at a crossroads. On the one hand, the Port would appear to be a prosperous and growing enterprise. It is the largest petroleum importer in the country and the third largest Port in the United States (largest on the east coast) in terms of cargo volume. However, behind these seemingly encouraging statistics lies a serious and growing problem. Though the Port has grown it comes at a time of overall shipping growth worldwide.

A.5.4 Selection process of potential decontamination technologies

The objective was to identify, test, evaluate and select technologies for the treatment of contaminated estuarine sediments which facilitate the disposal of navigationally- dredged sediments from the New York/ New Jersey Harbour. Technologies were evaluated based on criteria outlined below;

Technical evaluation criteria will carry the greatest weight in selecting the contractors. These criteria will be point scored and are given below in descending order of importance.

- Treatment process effectiveness (15%),
- Project specific applicability (10%),
- Potential beneficial use of end products (8%),
- Environmental impacts (7%),
- Treatment technology overview (5%),
- Process description (5%),
- Environmental health (5%),
- Safety, quality assurance (5%),
- Organisational experience (10%),
- Personnel (5%),
- Facilities (5%).

Selected technologies will be required to demonstrate via bench-scale testing the efficacy of the sediment decontamination. Effective bench-scale technologies will then be considered for the operational pilot-scale testing. This RFP is aimed at fast-track investigations of technologies capable of meeting these criteria and which presently operate or can be reasonably anticipated to operate at the pilot scale in 1995.

A two phase program is planned:

- Phase I Technical evaluation and bench scale testing
- Phase II Optional pilot scale testing

A.5.4.1 The technologies

A number of vendors came forward.

USEPA and USACE were authorised to jointly conduct an investigation and demonstration of decontamination technologies applied to contaminated NY/NJ Harbour dredged material. USDOE Brookhaven Laboratory (BNL) is providing technical support and serves as the procurement agency.

The project undertaken by USEPA, USACE and USDOE Brookhaven National Laboratory (BNL) involves bench-scale testing with pilot-scale demonstrations of selected processes, along with ancillary studies (e.g. Phase I sediment TIE, beneficial use evaluation, treatment-train development, and preliminary risk assessment.)

Twelve processes were tested in the laboratory, where 5-10 gallons of dredged material each were processed. Participants were WES, Battelle, and seven commercial vendors under BNL RFP procurement.

Based on bench-scale results, five of the processes were selected for pilot-scale demonstrations. Pilot demonstrations processed up to 25 yd^3 each.

The pilot demonstrations are as follows:

- Institute of Gas technology tested at Golden, CO a thermochemical process using a rotary kiln. The end product is a pozzolanic material which can be mixed with portland cement to make a marketable blended-cement product. Pilot demo was completed in November 1996.

- Metcalf and Eddy tested two systems at Port Newark, NJ:

    - 1) a solvent-extraction process followed by cement stabilisation; and

    - 2) stand-alone cement stabilisation. Pilot demos were completed in November 1996.

- Westinghouse Science and Technology Center tested a thermal vitrification process at Madison, PA using a plasma melter. The end product is a glass-like material which can be further processed to make glass-fibre products. Pilot demo was completed in December 1996.

- WES is testing at Port Newark a manufactured-soil production followed by phytoremediation (i.e. using grass and other plants to clean up or stabilise contaminants). Pilot demo will continue until May 1997 to evaluate winter kill of vegetation.

Potential beneficial uses of treated material, in addition to those noted above include construction fill, construction aggregate, roadbase material, mine reclamation, brownfield reclamation and landfill cover.

Commercial-scale pilot demonstrations for processing 10,000 to 500,000 CY using funds from the Port Authority and the States of NY and NJ.

The selection of unit process technologies to be utilised in the overall treatment strategy for the Harbour sediments will be dependent on a number of factors, including, but not limited to:

- Suite of contaminants to be treated
- Volume of sediments requiring treatment
- Treatment efficiency requirements
- Volume and nature of residuals from selected treatment process
- Secondary treatment requirements
- Treatment costs
- Compatibility of treatment processes
- Public/ community acceptance requirements

- Treatment site limitations, including site size requirements
- Health and safety concerns of selected treatment method

Appropriate evaluation of the sediment contamination and the site is essential in a remediation trial. High costs of sampling and analysis frequently result in insufficient information and data from being gathered.

An evaluation programme dealing with the need to treat dioxin contaminated sediments from NY/NJ sediments. Often grouped in the following general categories; biological, extraction, stabilisation/solidification, radiant energy, chemical and thermal technologies. Following a detailed evaluation and bench scale testing the following three technologies were selected for further evaluation.

- Base-catalysed decomposition (chemical treatment technology)
- Rotary Kiln incineration (thermal treatment technology)
- BEST solvent extraction (extraction technology)

Solidification and stabilisation
This process is being commonly applied. Economies of scale and greater expertise mean that the costs of stabilisation and solidification in the USA have fallen considerably since introduction of this process.

A.5.4.2 Approach to the solution of clean-up
The approach recognised the need for immediate solutions to contamination so that port operations could continue to function and the need to develop the best solutions for the longer term. Two phases to the study were adopted. in addition, vendors were invited to display and justify the validity of their technology. This put the emphasis on them to sort out the technical aspects. It was recognised that the selection of technologies for the solution to the NY/NJ contaminated dredged material disposal problem would involve treatment trains and also the dredging process (dredging method and transport) as the properties of the dredged material (physical and chemical) would effect which technologies were needed.

This put the emphasis on them to sort out the technical aspects. It was recognised that the selection of technologies for the solution of the NY/NJ contaminated dredged material disposal problem would involve treatment

A.5.5 Pilot projects

PORT NEWARK SITE, NEW JERSEY, USA

A pilot project was set up using the solidification and stabilistation technology. Two binders were selected because of their non proprietry nature and ready availability:

- Portland Cement
- Lime/ fly ash

The Newark project is an example of an ex-situ stabilisation and solidification process, where direct cement addition and mixing is used to treat contaminated sediments. Thousands of cubic metres of sediment with low level organic and inorganic contamination are dredged daily from the Ports of New York and New Jersey. Barges are filled with sediment and are taken to a recycling facility in Port Newark.

The dredged material naturally has low cohesion and strength. However, stabilisation and solidification is being used to transform the chemical and physical properties of the material, creating an engineered structural fill. the mixing equipment is able to thoroughly blend a cement slurry within the barges and therefore dewater the dredged sediments. The project is using some 20,000 tonnes of cement per week. It is anticipated that around 450,000 tonnes of cement will eventually be used. In excess of 40 million m^3 of dredged material is likely to be produced from the New York and New Jersey harbour channels.

The structural fill is stockpiled before being transported by lorry a few miles to a reclamation site. there it is spread and compacted. When completed the site will be used as a shopping mall, with a large adjacent parking lot. Further contracts are expected to be awarded using this process. Fortunately there is a considerable area of derelict ex Defence Department land available which can accommodate the treated silt. The land is nearly all ear marked for redevelopment.

The contractor has developed specialist (patented) mixing equipment which ensures that the cement slurry is blended efficiently with the dredged silt.

Overall there will be a total of 1 to 2 M cu yards of dredged material "beneficially" used at this site.

A.5.6 Approach

The study was conducted in five phases:

1. Sample collection. This was performed by the US Army Engineer District New York. Samples were composited and shipped to WES Vicksburg for analysis;
2. Screening tests. Initial screening tests were performed to narrow the range of binder dosages and water to sediment ratios for preparing the test specimen. Moisture contents were evaluated to determine whether the addition of water was necessary and to evaluate the success of homogenisation efforts.
3. Preparation of test specimens for detailed evaluation. The sediment was mixed with binders and cured under controlled conditions.
4. Physical and chemical testing. Based on the results of the UCS and toxicity charecteristic leaching procedure (TCLP) leachability of metals, specimens were selected fro detailed evaluation of contaminant leachability.
5. Report preparation. Results from the physical and chemical tests were used to develop conclusions.

A.5.7 Pilot study conclusions

The study showed that common generic binders can be applied to New York/New Jersey Harbour sediments to alter the physical and chemical properties of the sediment.

Specific conclusions are as follows:

- Cement and lime/fly ash treatment of the sediment substantially increases the handling properties of the sediment.
- The cement treatment was more effective in producing material that developed better physical properties than the lime/fly ash developed material that have good physical properties.
- All BSRs evaluated increased the volume of the sediments that must be handled.
- The optimal binder formulation was 0.4 cement and 0.3/0.6 lime/fly ash.
- The results of the TCLPP performed on the optimal formulations indicated that the treatment reduced leachability for most contaminants evaluated.
- The data indicate that binder ratios of 0.4 cement and 0.3/0.6 can effectively solidify/stabilise the New York/New Jersey Harbour sediment.

A.5.8 General conclusions

The feeling in America is that the handling of the material and demonstrating end uses (beneficial use with a continuous supply of dredged material and a consistent use of the product) are vital in the whole management of dredged material and specifically in the use and development of treatment technologies. It is strongly believed that the treatment methods may be thought of as a black box which will resolve itself by the vendors sorting out the engineering and technical difficulties. This can only happen if the beneficial use or final placement option is clearly demonstrated and communicated.

Black box- Contractors will work out the technical and engineering aspects of decontamination technologies. They will continue to work at a technology if the contract is kept open. In US they are doing this. It also sorts out the cowboys (and there may be a high percentage of these) from the companies with promising technologies. In the NY/NJ programme they selected 6 to 8 technologies from an application of approximately 600. Working relationships are also important.

PRPs- principle (potential) responsible parties once highlighted for a site are doing the most in tracking down source inputs and spending money on sediment monitoring programmes. It is within their interest to do so.

It is important that decisions are documented, even if the result is no action.
Options are no action, treatment, containment and disposal.

Appendix 6

List of companies offering de-contamination

Appendix 6 List of companies offering de-contamination

Disclaimer
The following list of technologies and suppliers has been compiled from published literature and trade brochures. It is provided to assist potential users in their search for solutions to specific problems. Presence in this list does no imply any endorsement by the authors of either the supplier or the technology.

Categorised by treatment process

1. PRE-TREATMENT

1.1 Dewatering
No information

1.2 Separation
No information

2. THERMAL DESTRUCTION

2.1 Incineration

Rotary Kiln

Aqua-Guard Technologies, Inc. (Vancouver, BC)
  Aqua-Guard Thermal Oxidation
Bruce Brown Associated Ltd (Toronto, Ontario)
  BA Brown Thermal Oxidation
Vesta Technology Ltd (Fort Lauderdale, Florida)
  Vesta 100 Incinerator
Chemical Waste Management Inc (Oak Brook, Illinois)
  PYROX Transportable Thermal Destruction System
BOVAR Environmental Services (Calgary, Alberta)

ENSCO (Williamsville, New York)
  Modular Waste Processor

Fluidised Bed

Jan de Nul (Aalst, Belgium)
  DJN Zerofuel Fuid Bed Sludge Incineration
Morrison Knudsen Corp (Boises, Idaho)
  MK Thermal Treatment Units
Ogden Environmental Services (San Diego, California)
  OES Circulating Bed Combustor Incinerator

Infrared (SHIRCO)

OH Materials Corp (Findlay, Ohio and Oakville, Ontario)
  OHM Mobile Infrared Incineration Systems

Innovative Incineration technologies

Babcock & Wilcox (Allience, Ohio)

Cyclone Furnace. Pilot scale only; all organic compounds: feed material must be screened and dry. Produces Vitrified slag.

Energy and Environmental Research Corp (Irvine, California)

EER Spouted Bed (Hybrid Fluidised Bed). Pilot scale only; all organic compounds; suitable for 40-50% moisture content. Produces ash.

Institute of Gas Technology (Chicago, Illinois)

Two-stage incineration. Pilot scale only; all organic compounds; feed material must be screened. Produces vitrified pellets.

EnviroTech BGF (Montreal, Quebec)

Plasmawaste/Plasmadestruct. Used in Sweden.; all organic compounds. Produces slag.

American Combustion Inc (Norcross, Georgia)

Pyretron Oxygen Burner. Pilot scale only. Secondary burner for any incinerator; treats off-gas only. Residue is ash.

Retech Inc (Ukiah, California)

Plasma Centrifugal Furnace (Plasma Arc Vitrification). Full scale prodcution up to 1.1 tonne/hr. All organic compounds: feed material must be screened. Produces vitrified slag.

Allis Mineral Systems Inc (Milwaukee, Wisconsin)

Pyrokiln Thermal Encapsulation. Pilot scale only. All organic conpounds and metals. Produces slag.

VORTED Corp (Collegeville, Pennsylvania)

Oxidation and Vitrification Process. Pilot scale only. All organic compounds and metals. Produces vitrified slag.

Horsehead Resource Development Comp (Monaca, Pennsylvania)

Flame Reactor Process. Pilot scale only. Metal-contaminated solids; low moisture, finely screened. Produces vitrified slag.

ELI Eco Logic International (Rockwood, Ontario)

Thermal Gas Phase Reduction Process. Pilot scale only. All organic compounds. Produces grit and slag.

2.2 High Pressure Oxidation

Wet air oxidation

Zimpro Passavant (Rothschild, Wisconsin)

Supercritical water oxidation

Modar Inc (Natick, Massachusetts)

Uses high pressure pumps and an above-ground reactor.

VerTech Treatment Systems (Air Products and Chemicals, Allentown, Pennsylvania).

Uses a well between 2,500 and 3,000m deep to achieve the necessary pressures.

2.3 Vitrification

Vitrifix NA (Alexandria, Virginia)

Developing full-scale unit for asbestos.

Geotech Development Corp.

No details available

Penberthy Electromelt

No details available

Geosafe Corp., (Kirkland, Washington).

In-situ vitrification patented.

Heijmans Milieutechniek BV (PO Box 377, 5240 Rosmalen, Netherlands)

Artificial basalt process

Gemco Engineers BV (PO Box 1713, 5602 BS Eindhoven, Netherlands)
Artificial basalt process
Techno Invent BV (Vliegerlaan 35, 7313 GW Apeldoorn, Netherlands)
Artificial basalt process

3. THERMAL DESORPTION TECHNOLOGIES

Rust Remedial Services, Inc (Oak Brook, IL)
Fuel conversion system, uses steam or hot oil heated thermal screw. Available full scale.

Texarome, Inc. (Leakey, TX)
Mobile solid waste desorption, uses superheated steam. Pilot scale only.

Western Research Institute (Laramie, WY)
Recycle Oil Pyrolysis and Extraction (ROPE^R) uses heated thermal screw. Pilot scale only.

Westinghouse Remediation Services, Inc.
Westinghouse Infrared Thermal Desorption Unit, uses infrared heating rods on a steel belt conveyor. Available full scale.

Ariel Industries, Inc. (Chatanooga, TN)
Ariel SST Low Temperature Thermal Desorber, uses rotary drum dryer. Available full scale.

Carson Environmental (Los Angeles, CA)
Heated paddle augers with UV light and with ozone and hydrogen peroxide circulated above thesoil. Pilot scale only.

Cleansoils Inc. (New Brighton, MN)
Thermal Desorber. No details available. Available full scale

Conteck Environmental Services, Inc (Elk River, MN)
Uses rotary drum dryer. Available full scale.

CSE Inc. (Roseville, MN)
Thermal Desorber. No details available. Available full scale.

DBA, Inc. (Livermore, CA)
Uses rotary kiln. Available full scale.

Enviro-Klean Soils, Inc. (Snoqualmie, WA)
The Klean Machine, uses direct heating. No details on availability.

Hazen Research, Inc and The Chlorine Institute (Golden, CO)
Uses stationary hearth or rotary furnace (for mercury removal). Pilot scale only.

Hrubetz Environmental Services, Inc. (Dallas, TX)
HRUBOUT^R, uses hot air injections and recovers (possible CDF application). Available full scale.

IT Corporation (Knoxville, TN)
Uses indirectly heated rotary drum. Pilot scale only.

Kalkaska Construction Service, Inc. (Kalkaska, MI)
Uses rotary drum dryer. Available full scale.

Mittlehauser Corp (Naperville, IL)
Astec Thermal Desorption Unit, uses rotary drum dryer. Available full scale.

OBG Technical Services Inc.
Low temperature Thermal Desorption (LTTD), uses rotary drum dryer. Available full scale.

Thermatek Remediation Technologies (RETEC), Inc. (Concord, MA)
Uses Molten salt heated screws (augers). Available full scale.

Roy F Weston, Inc. (Westchester, PA)
Low Temperature Thermal Treatment (LT^{3R}), uses hot oil heated screws (augers). Available full scale.

Chemical Waste Management (Geneva, IL) *& Rust Remedial Services, Inc.* (Anderson, SC)
X*TRAX^{R}, uses indirectly heated rotary dryer. Available full scale.

Seaview Thermal Systems (Blue Bell, PA)
HT-V Thermal Distillation, available full scale.

Separation and Recovery Systems, Inc. (Irvine, CA)
SAREX MX-1500/2000/2500, use indirect heating. Available full scale.

Soil Purification, Inc. (Chatanooga, TN)
Astec Soil Purification LTTD, uses rotary dryer. Available full scale.

Soil Tech ATP Systems, Inc. (Englewood, CO)
SoilTech ATP System, uses indirectly fired rotary kiln. Available full scale.

Southwest Soil Remediation, Inc. (Tucson, AZ)
Low Temperature Thermal Desorption, uses rotary dryer.

Thermotech Systems Corp (Orlando, FL)
Tandem SRU, available full scale.

Recycling Sciences International, Inc (Chicago, IL)
Desorption and Vapourisation Extraction System (DAVES^{R}), uses fluidised bed. Available full scale.

Canonie Environmental Services, Inc. (Porter, IN)
Low Temperature Thermal Aeration (LTTA), uses rotary dryer, direct fire. Available full scale.

Agglo Recovery, Inc. (Rexdale, Ontario)
Agglo Activated Thermo-chemical Process, uses fluidised bed and vacuum distillation. Pilot scale only.

NBM Bodemsanering BV (Netherlands)
Indirectly-heated Thermal Desorption, uses indirectly heated rotary dryer. Available full scale.

OHM Materials (Findlay, OH)
OHM Mobile Thermal Volatilisation System (MTVS), available full scale.

Laidlaw Waste Systems, Ltd (Burlington, Ontario)
The Soil Recycler, available full scale.

Remco Environmental Service Ltd. (Surrey, British Colombia)
Thermal Soil Treatment Process, uses indirect heat and steam. Available full scale.

Vesta Technology, Ltd (Ft Lauderdale, FL)
VESTA Thermal Desorption, uses rotary kiln. Available full scale.

4. IMMOBILISATION TECHNOLOGIES

Physical immobilisation

No information but see also vitrification in Section 2.

Chemical immobilisation

MBS process (Molecular Bonding System)
Solucarp Industries Ltd, W Nyack, New York (UK Tel 0151 645 7571) Immobilises heavy metals.

SILT NV – In situ immobilisation by injection of proprietary chemicals

5. EXTRACTION TECHNOLOGIES

Acid Extraction Treatment System
Extracts metals using unspecified acids

ALTECH Mobile Soil Washer
Extracts all organic compounds and all inorganic compounds.

ARC/EPRI Clean soil process
Extracts hydrocarbons using fine coal particles.

ASRA-DEMI Process
GKSS Forschungszentrum Geesthacht GmbH, 21502 Geesthacht, Max Planck Strasse.
Separates silt fraction and organics from mineral solids by high energy washing under parlty cavitating conditions.

Basic Extractive Sludge Technology (BEST^R)
Extracts specified organic compounds using triethylamine.

Beak Eaxtraction with Methanol
Extracts specified organic compounds using methanol.

BioGenesis Soil Washing Process
Extracts hydrocarbons using unspecified medium.

Biogenie Physico-Chemical Extraction
Extracts all inorganic compounds using unspecified medium.

Carver-Greenfield
Extracts specified organic compounds using food-grade oil.

CF Systems Solvent Extraction
Extracts all organic compounds using propane.

COGNIS Coupled Metal Extraction
Extracts all metals using unspecified medium.

Desorption & Vapour Extraction System
Extracts hydrocarbons, volatile organic compounds using a thermal method.

Dravo Rotocel
Extracts hydrocarbons using unspecified medium.

Ecotekniek Extraction
Extracts hydrocarbons using unspecified medium.

Electrokinetic Soil Processing
Specified organic compounds, specified inorganic compounds, metals using electro-osmosis.

Extraxol
Extracts hydrocarbons using an organic solvent.

Ghea Extraction
Extracts all organic compounds and metals using surfactants.

Heavy Metal Extraction Process
Extracts metals using acid and ion exchange technique.

IGT Extraction
Extracts specified organic compounds using supercritical gas.

IHC Metal Extraction
Extracts metals using acid or complexing agents.

In-Pulp Extraction Process
Extracts all organic compounds and metals using carbon-in-pulp and resin-in-pulp resins.

Low Energy Extraction Process
Extracts all organic compounds using hydrophilic leaching solvent and hydrophobic stripping solvents.

Mackie Vat Leaching Jig
Extracts metals using unspecified medium.

MBI Metal Extraction
Extracts metals using unspecified acid.

METALEX
Extracts metals using unspecified medium.

Metanix Technology
Extracts metals using unspecified solvent and chelating agent.

Modular Vapour Extraction System
Extracts volatile organic compounds using air and vacuum technique.

NRCC Adsorption Approach
Extracts all organic compounds using coal, shredded rubber or other adsorbents.

Oleophilic Sieve
Extracts hydrocarbons and metals using oleophilic surfaces.

Sequential Metal Leaching System

E£xtracts metals using hydrochloric acid and chelating agent.

Solvent Extraction Sand Agglomeration

Extracts hydrocarbons using an oil displacement mechanism.

SILT Extraction

Unspecified

Soil Restoration Unit

Extracts all organic compounds using a range of unspecified solvents.

Solvent Extraction for Dredged Soils

Extracts specified organic compounds using a polar/non-polar mixture.

Texarome Process

Extracts volatile organic compounds using superheated steam.

Thorne Vapour Extraction System

Extracts volatile organic compounds using vacuum extraction.

University of Wisconsin Extraction

Extracts all organic compounds using surfactants and solvents.

VITROKELE Soil Remediation Technology

Extracts all inorganic compounds and specified organic compounds using various unspecified leaching agents.

6. CHEMICAL TREATMENT

No information

7. BIO-REMEDIATION TECHNOLOGIES

International Bioremediation Services Ltd

Bio-logic Remediation Works Ltd

Biologix Environmental Ltd

Veridian

EA Technology Ltd?

Environmental and Biosafety Services

SILT NV

Celtic Technologies

Biolytic systems Ltd

Land and Water Services

BHR Group Ltd?

Bio Chemical Technologies, Loosterwerg 33, Voorhout, Postbox 35, 2170 AA Sassenheim, Holland.
Biofixation technique.

Storm Environmental Consultancy (SEC), Groningen, Netherlands
BiMicrobial Metaleaching^R for removal of heavy metals

GRACE Bioremediation Technologies, 3451 Erindale Station Road, Mississauga, Ontario, Canada L5A 3T5.
DARAMEND^R for application to landfarming, demonstrated effective for PAH's.

DHV Milieu en Infrastructure BV, Postbus 1076, 3800 BB Amersfoort, Netherlands
Fungi Farming^R demonstrated effective for mineral oil and PAH.

Heidemij Realsatie BV, PO Box 660, 5140 AR Waalwijk
FORTEC^R demonstrated effective for PAH and mineral oil

8. ELECTROKINETIC TREATMENT

No information